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Conversion of Organic Wastes to Unleaded, High-Octane Gasoline

(U.S.) Naval Weapons Center, China Lake, CA

Prepared for

Industrial Environmental Research Lab.
Cincinnati, OH

Jan 84

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CONVERSION OF ORGANIC WASTES TO UNLEADED, HIGH-OCTANE GASOLINE

by

James P. Diebold
Charles B. Benham - G. D. Smith

Naval Weapons Center
China Lake, CA 93555

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Project Officer
Walter W. Liberick, Jr.

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OH 45268

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PERFORMER: Naval Weapons Center, China Lake, CA.

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This project has demonstrated the marriage of two diverse technologies previously considered to be unrelated--the pyrolysis of organic wastes and the low-pressure polymerization of low-molecular-weight hydrocarbons to form polymer gasoline. This program comprised the development of a multistep chemical process to convert solid organic materials into a liquid hydrocarbon product consisting primarily of high-octane gasoline. This process selectively pyrolyzes organic wastes to form gases rich in reactive hydrocarbons such as ethylene and propylene. The pyrolysis gases are compressed and purified to result in three gaseous streams: carbon dioxide; by-product fuel gases (hydrogen, methane, and carbon monoxide); and reactive hydrocarbons. This last stream is further compressed and sent to the polymerization reactor where high-octane gasoline is formed.

KEYWORDS: *Organic compounds, *Solid waste disposal, *Gasoline, *Cellulose, *Refuse derived fuels, *Unleaded gasoline.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report covers the laboratory development of a multistep chemical process to convert solid organic materials into a liquid hydrocarbon product consisting primarily of high-octane gasoline. In the first step, organic wastes are pyrolyzed to form gases rich in reactive hydrocarbons. In later steps, these gases are compressed to concentrate the low-molecular-weight reactive hydrocarbons which subsequently are polymerized to form polymer gasoline.

Both governmental and private agencies interested in synthetic fuel development should find this report of value.

David G. Stephan
Director
Industrial Environmental Research
  Laboratory
Cincinnati, Ohio

PREFACE

The United States has based its transportation upon the availability of inexpensive, clean-burning energy in the form of petroleum-derived hydrocarbons. These petroleum products are liquids which are easily stored and have a large energy content on both a volumetric and a weight basis compared with other fuels or energy-storage systems. The petroleum liquids are easily metered into boilers or engines for precise control. In short, if petroleum liquids had not occurred naturally, they would have been invented for use, especially for mobile power needs such as for cars, trucks, and airplanes.

The increasing scarcity of petroleum products due to gradual depletion of oil supply should, over the long run, have the effect of steadily escalating the price of these products at a rate faster than the rise in the overall economy. Thus, synthetic petroleum economics will predictably improve with time. The scarcity of petroleum products could be magnified due to a large United States dependence on the importation of oil, the price and supply of which could be influenced by actions of foreign nations.

The relative value of commonly used fuels has a large impact on the preferred energy product. As an example of the value of commonly used fuels, consider that in 1975 if the cost to a commercial user of interruptible natural gas for boiler fuel was $1.00 per unit of energy, then noninterruptible natural gas for homes was worth $1.42 per unit of energy, the relative value of viscous No. 6 fuel oil for boiler fuel was $3.08 and the value of gasoline was $5.48. Recent relative increases in the value of natural gas have temporarily reduced the price ratio of gasoline to natural gas. However, the widely predicted future petroleum shortage could cause the value of gasoline to escalate at a rate much greater than that of boiler fuels. This difference will occur because, although coal can again become the primary boiler fuel for the nation, automobiles using coal, having today's performance are not available.

A synthetic petroleum source for transportation purposes will, therefore, be needed. The process developed in this program to produce synthetic liquid hydrocarbon fuels utilizes the replenishing resource of organic wastes, achieves a 95% reduction of the waste stream and is consequently environmentally beneficial. This process results in a synthetic product which is 90% high-octane polymer gasoline and 10% oils. For comparison, only the very best United States crude oils contain as much as 50% straight-run gasoline having only a low-to-medium octane rating. The synthetic polymer gasoline product can be mixed in all proportions with petroleum-derived gasoline, and the user will not be aware of any changes in appearance or performance. The light-oil product is a

mixture of Type JP-5 jet fuel, lubricating oils, and residual fuel oils. Development and commercialization of this proposed process could lessen the impact of petroleum shortages, and convert organic wastes into an asset.

ABSTRACT

This project has demonstrated the marriage of two diverse technologies previously considered to be unrelated--the pyrolysis of organic wastes and the low-pressure polymerization of low-molecular-weight hydrocarbons to form polymer gasoline.

This program comprised the development of a multistep chemical process to convert solid organic materials into a liquid hydrocarbon product consisting primarily of high-octane gasoline. This process selectively pyrolyzes organic wastes to form gases rich in reactive hydrocarbons such as ethylene and propylene. The pyrolysis gases are compressed and purified to result in three gaseous streams: carbon dioxide; by-product fuel gases (hydrogen, methane, and carbon monoxide); and reactive hydrocarbons. This last stream is further compressed and sent to the polymerization reactor where high-octane gasoline is formed. No catalysts are used in the process. A bench-scale system was built which demonstrated the selective pyrolysis, the gas purification, and the polymerization aspects of the process. Based upon experimentation at the Naval Weapons Center it is projected that about 0.28 liter of gasoline and 0.03 liter of oils per kilogram of organic material can be produced from municipal trash with this process (68 gallons of gasoline and 8 gallons of oils per ton).

This report was submitted in fulfillment of Interagency Agreement EPA-IAG-D6-0781 (as amended) between the Naval Weapons Center, China Lake, CA and the U.S. Environmental Agency's Industrial Environmental Research Laboratory in Cincinnati. This report covers the time period from June 1975 to January 1979; work was completed as of 12 January 1979.

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SECTION 1

INTRODUCTION

The possibility of an economical process to convert organic waste material into gasoline was identified at the Naval Weapons Center (NWC) in 1973 during a project funded by the Department of Defense Advanced Research Projects Agency (DoDARPA). The purpose of the project was to evaluate the feasibility of energy independency for remote military installations. In the course of this study,(4) possible utilization of the energy content of trash was intensely evaluated. Although direct combustion was considered for simple waste disposal, the feasibility of converting the organic wastes to a high-grade liquid fuel suitable for mobile transportation appeared to be advantageous in many respects. Two approaches were considered in detail: (a) pyrolysis of wastes to form reactive hydrocarbons (e.g., ethylene), and their subsequent purification and conversion to a synthetic hydrocarbon gasoline which could then be substituted for gasoline derived from petroleum sources with no changes in storage facilities, engine design, toxicity, or performance; and (b) pyrolysis of wastes to form a synthesis gas composed of carbon monoxide and hydrogen with subsequent catalytic conversion to methanol, which could then be used as a gasoline substitute after some distribution system and engine modifications. Both of these processes appeared to have considerable merit as economical methods to dispose of waste materials while producing an energy product. Contact with the Industrial Environmental Research Laboratory (IERL) of the Environmental Protection Agency (EPA) in Cincinnati, Ohio, resulted in funding, June 1975, EPA-IAG-D5-0781, to study the conversion of organic wastes to gasoline.

The critical technology that this program needed to demonstrate was in the area of selective pyrolysis of cellulosic organic waste materials into gases containing large amounts of olefins and their subsequent processibility. If the selective pyrolysis could be verified and demonstrated, then the remainder of the process to make gasoline was thought to be relatively straightforward from the industrial experience with similar processes. In effect, the process would parallel that of an oil refinery, with the most significant difference being the use of cellulosic waste material rather than crude oil as feed stock.

A continuous bench-scale system for the conversion of powdered (ECOII)* municipal solid waste (MSW) to gasoline was constructed and operated with promising results. Projected yields are on the order of 28 decaliters (75 gallons) of gasoline crude per ton of dry, ash-free organic waste or about 17 decaliters (45 gallons) of gasoline crude per ton of MSW. Small amounts of diesel oil and lubricating oils would be the only by-products, except for the ash contained in the feedstock. Char, tar, and by-product gases such as hydrogen, methane, and carbon monoxide may be combusted to maintain the energy independence of the process. About half of the energy contained in the organic waste materials fed to the process can appear in the hydrocarbon fuel product. Overall, this process removes the oxygen from cellulosic wastes to produce a gasoline consisting of hydrocarbons. Most of the rejected oxygen is eventually in the form of carbon dioxide.

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* ECOII is a treated solid waste using a proprietary process changing its physical characteristics to that similar to coal, brittle and "crystaline like".

SECTION 2

CONCLUSIONS

The overall process to convert organic waste materials into high-octane gasoline appears to be very promising based on the experimental work conducted during this program. The pyrolysis of organic wastes to produce the necessary ethylene and propylene required for high yields of gasoline or petrochemicals was demonstrated. With respect to purification of the pyrolysis gases, the very selective removal of carbon dioxide was achieved. The separation of the by-product fuel gases from the desired olefins was demonstrated to have promise, but the desired high purity of olefins was not obtained as yet when the experimental work was terminated.

Polymer gasoline was made in a small-scale reactor from pure ethylene to gain insights into the exothermic reaction. The resultant crude oil contained 85 to 90% gasoline, which tested out at 90 octane using the ASTM motor method. Polymer gasoline made from the partially purified pyrolysis gases has similar physical and distillation characteristics to that made from ethylene. The presence of carbon oxides and methane in the polymerizer served only to slow the reaction, but hydrogen reacted quite readily to form the nonreactive, saturated ethane, propane, and butane. The preliminary economic projections made for the process were based on an outside consultant's evaluation and appeared to be very promising. Further process development study at the bench and pilot-plant scale should provide greater accuracy in the economic projections. Additional work must be performed at the bench scale before the pilot plant is designed. Given the length of time for a continuous, orderly development, the first commercial plant could be operational in 6 to 7 years.

SECTION 3

RECOMMENDATIONS

BENCH SCALE

The concept of converting organic waste material to high-octane gasoline has come a very long way from the initial paper study. A bench-scale system has demonstrated initial technical feasibility of the concept. This small-scale system is thought to be unique in its overall capabilities. However, the confidence level in the design of a scaled-up pilot plant would be greatly enhanced if the integrated bench-scale system, somewhat modified, were to be operated on a continuing basis to provide more detailed information. A future program should look at system optimization or tuning, organic by-product disposal, and alternate feedstock evaluation.

With completion of the integrated pyrolysis-purification-polymerization system, an in-depth study of process variables could be conducted. The study's goal would be to verify expected interactions and to reveal unexpected interactions which impact on the pilot-plant design. The results of this study would help to better establish the desired versatility in the operating capabilities of the pilot plant. It is thought that the pyrolysis system has been relatively well optimized for the production of desired olefins from ECO II.

The elimination of fine char, tar vapors, and carrier steam from the raw pyrolysis gases has progressed a long way. If the tar vapors are cooled in the tubing to their dew point, the dilute tar vapors would precipitate out and solidify at that cool location. The reason for going to a two-stage spray-tower approach (the quench drum and the demister) was to remove these contaminants so that the tars could cool and solidify without adhering to the wall of the connecting tubing. This approach has been relatively successful, but a fine mist of water and tar still has been collecting on the inside of the connecting tubing and on the filter located near the compressor inlet. If the tars enter the compressor, they cause the compressor valves to stick. Additional work is recommended to devise a system that more completely eliminates this mist from the pyrolysis gas stream. Electrostatic precipitation techniques in combination with the spray towers and/or a redesign of the spray tower may be applicable. Improvement in this portion of the system will decrease the time spent in equipment cleanup between pyrolysis runs and provide additional information for scale-up.

In the high-pressure gas purification area, process variables having a large impact on the pilot-plant design are pyrolysis gas flow rate, the ratio of hot carbonate solution to pyrolysis gases, the heat input to regenerate the carbonate solution, the ratio of lean oil to pyrolysis gases, and the estimated heat input to regenerate the lean oil. These variables should be investigated to ensure good purification performance for the bench scale and to provide design data for the pilot plant.

So far there has been limited experience with the operation of the high-pressure gas purification system, but some contamination may accumulate in the hot carbonate as well as in the hydrocarbon absorption systems. The extent of these problems and their resolution will need to be addressed as they are observed. Because of the moderately high temperatures in the hydrocarbon stripper, some of the butadienes absorbed in the lean oil apparently polymerize to form gums and tars. Some of these tars remain in solution, so that the lean oil needs to be periodically cleansed by distillation techniques. It is recommended that the possibility be investigated of designing the hydrocarbon stripper so that the high-molecular-weight gums and tars may be concentrated and separated from the lean oil without the requirement of a separate distillation column. This approach appears feasible, since the hydrocarbon stripper is a packed column and the bottom third is operated near the boiling point of the lean oil. If a distillation "tray" is located near the bottom of the stripper and the lean oil removed from this tray, the gums will tend to collect in the very bottom of the column, from which they may be withdrawn in a concentrated form. Otherwise, the dirty lean oil will periodically need to be removed, distilled, and returned to the system. More experimentation is needed to tune the hydrocarbon absorber and stripper to produce the purity of gases desirable.

In the polymerization area, variables of interest that will affect the pilot-plant design are: ethylene to propylene ratio in the polymerizer feed gases, temperature, residence time, and the recycling of unpolymerized gases. The polymerization subsystem in theory should behave very similarly to those systems reported in the literature, since the feed gases should be nearly all hydrocarbons. However, most of the operating data reported 3 to 4 decades ago was for feed gas streams predominately composed of propylene and butylenes as opposed to primarily ethylene and propylene. Since ethylene is more exothermic and has a much greater rate of polymerization reaction than the larger olefins, extra care will be needed to assure that the polymerizer reactor will be maintained at a reasonable temperature. Changes in the ethylene-to-propylene ratio in the feed gas will affect the polymerization rate, the reactor heat load, and the necessary heat removal rate. Recycling the uncondensed gases (containing some methane, ethane, and propane) from the gasoline accumulator will tend to dilute the system to both slow the polymerization rate and act as a heat sink to help moderate the temperatures. These polymerization process variables should be investigated so that valid recommendations can be made for the pilot-plant design. Samples of the crude gasoline should be sent to a petroleum laboratory for characterization.

The development of the trash-to-gasoline process is a relatively unusual program here at the Naval Weapons Center since most of the local effort is directed toward naval weapon systems development. Consequently, the trash-to-gasoline program has developed in a relatively isolated environment with a steep learning curve involved, particularly in bench-scale equipment selection.

It would be desirable to use the consulting services of a petrochemical or petroleum firm engaged in process development. The consultant would evaluate the bench-scale system to make suggestions for improving its operation and for ensuring that the operating data will be meaningful for scale-up to the pilot plant. Recommendations for the goals and scope of the pilot plant should be made, as well as realistic mass and energy balances and a preliminary cost estimate for the pilot-plant phase.

Ideally, the process will produce only the liquid hydrocarbon fuel products, water vapor, carbon dioxide, waste heat, and ash. However, the pyrolysis process converts the organic material into about 75 to 80% gases, 15 to 18% char, and about 5 to 7% tars and water-soluble organics. The disposal of the char will be by combustion similar to that used for powdered coal. The contaminated water from the quench drum in the pyrolysis system has been used as boiler water to make "superheated steam" for the pyrolysis reactor. This contaminated water contains soluble organics (e.g., phenols), insoluble tar particles, and very fine char particles which escape the char cyclone. In addition, the water derived from the moisture content of the feed and an estimated very small amount of water formed by pyrolysis will accumulate in the system. The disposal of the tars, water-soluble organics, and excess water (if any) needs further experimentation since these by-products could have an adverse environmental impact.

The compressor condensate is a dark, thin liquid having two phases (presumably aqueous and organic) which have extraordinary solvency power. It is suspected that the organic phase consists primarily of aromatics such as benzene, toluene, xylene (BTX), and ethylbenzene based on other pyrolysis efforts. The aqueous phase is thought to contain water, acetone, methanol, acetic acid, formaldehyde, and other components. The liquids have an odor indicative of sulfur compounds and are thought to include the very small amount of hydrogen sulfide contained in the low-pressure pyrolysis gases since it is not present in the gas phase after compression according to gas chromatography. It would be desirable to use the organic phase as part of the gasoline product as is commonly done with aromatics by industry. Even with this addition of aromatic material, the product gasoline will have a fairly low total aromatic content since the polymerization reaction is expected to be operated below the aromatic forming temperatures. Since these aromatics have octane ratings of 100 or above, their addition will increase the octane level of the product in a manner identical to that of the aromatics formed in oil refineries during catalytic reforming to increase the gasoline octane value. It is recommended that the condensates found in the compressor and the surge tank be identified so that their usage and/or disposal can be established. This task will include the identification of a possible treatment of the liquids to remove the foul odors, preferably in an insoluble form suitable for land fill and/or by pyrolysis.

It is recommended that studies be made of the pyrolysis of undesirable organics found in the quench water and also of the feasibility of using the relatively slow water-gas reaction to eliminate unwanted water and char, while making superheated steam in the pyrolysis steam boiler. The initial mechanical feasibility of using the contaminated quench water for boiler water has been demonstrated, but the extent of the desired "cleansing reactions" to form gaseous products has not yet been evaluated. These "cleansing reactions" are thought to be as follows:

$$\text{Refractory organics} \xrightarrow[\text{pyrolysis}]{\text{severe}} CO + H_2 + C_{(s)} + CH_4$$

$$H_2O + C_{(s)} \xrightarrow[\text{gas}]{\text{water}} CO + H_2$$

The experiments would use quench water containing organics which had previously passed only once through the pyrolysis reactor. The pyrolysis system would then be operated with no fresh feed, but with the contaminated water being pumped to the boiler and subjected to the further pyrolysis step.

The severe pyrolysis of the more refractory organics by an additional pyrolysis step in the pyrolysis boiler will involve longer residence times and possibly higher temperatures than are used in the original pyrolysis step. These conditions will also encourage the relatively slow water-gas reaction to be more significant. The extra carbon monoxide, methane, and hydrogen formed by this second pyrolysis step would be beneficial as they will act as inert diluents and reduce the steam requirement in the initial pyrolysis step. This conversion to fuel gases of the tars, water-soluble organics, and fine char will greatly reduce the cost of handling and disposing of these by-products in full-scale plants.

In addition to the pyrolytic elimination of the undesirable fine char and organic material, their incineration in the pyrolysis furnace should be examined experimentally. Since the amount of contamination is relatively small compared with the amount of by-product gas and char burned in the furnace, the incineration of the contamination would have very little effect on the energy balances of the furnace. In fact, if the fluid fed to the furnace contained about 18% organic material, virtually no impact would be observed, since the heat of combustion of the organics would about compensate for the heat of vaporization and sensible heat absorbed by the water. It may well turn out that both the pyrolysis in the steam boiler and the incineration in the furnace will be needed in the process for environmental acceptability. The organic content of the quench water and its heat of combustion should be determined so that the feasibility of disposal by incineration can be projected. This experimentation would sample quench water which had been recycled several times to accumulate the more refractory organic compounds. The results from this sampling will be needed for the preliminary evaluation of the incineration of organic-containing waste water which otherwise could have an adverse environmental impact if not properly treated.

The pyrolysis experimentation in this program used ECO II as the feedstock. This material is derived from municipal waste and undergoes some degree of degradation during processing due to a combination of thermal and chemical action to embrittle the paper fraction before it is ground. It may be more desirable to build the pilot plant to process sawdust or other biomass-derived materials rather than MSW. Although there are many fairly large MSW processing plants under construction or in the early phases of operation, most of these plants have experienced severe operating problems due to the wide variety of materials discarded by society. For the purpose of process demonstration it may be desirable to use relatively uniform biomass feedstocks rather than MSW, particularly since the major potential for the process is with biomass rather than MSW. At least two biomass feedstocks thought to have different potentials for conversion to gasoline should be evaluated so that the versatility of the process and its potential for widespread deployment can be better predicted. Significant increases in gasoline yields are expected with feedstocks such as pine sawdust and walnut shells which contain fats, oils, or pitch, since these compounds are largely hydrocarbon in composition. For comparison, a biomass feedstock containing relatively low amounts of hydrocarbons, such as grass or poplar sawdust, should be evaluated. The selected biomass materials should be run through a pyrolysis test series to verify the optimum pyrolysis conditions. Then a quantity of gasoline for characterization should be produced from each of the biomass materials. The crude gasoline samples should be sent to an independent petroleum laboratory for testing. It is expected that the quality of the gasoline crude will be relatively constant, but that projected yields will vary considerably between the selected feedstocks. This evaluation will directly influence the pilot-plant siting and also will increase the level of confidence in the estimated potential impact the process can have for the economy of the United States.

PILOT PLANT

The scale-up of the process from the current bench scale to a commercial scale should probably involve an intermediate pilot scale. The preliminary draft of the evaluation of the trash-to-gasoline process (made by Dow Chemical Company under EPA Contract 68-03-2568-WDT-7003) suggested that a 20-ton/day pilot plant should be constructed. This size was thought to be large enough to provide good scaling information and highly accurate mass and energy balances. The cost of constructing such a pilot plant would appear to be in the \$3M to \$5M range, and the plant would cost about \$1M per year to operate. The length of desirable pilot-plant operation was not recommended in the study, but the time could easily extend for 2 years more than the 2 to 3 years required for construction. Thus, the cost of the pilot-plant phase would be in the neighborhood of \$5M to \$7M over a period of 4 to 5 years. Significant savings in time and cost are thought to be possible by contracting the pilot plant to a petroleum or petrochemical company experienced in piloting new processes of a similar nature. These companies would have in-house expertise to maximize the use of state-of-the-art techniques and equipment for the pilot plant. Much of the process equipment needed (e.g., packed towers, pumps, compressors, instrumentation, etc.) might not need to be purchased specifically for the program. Thus a well-staffed and equipped developmental facility could proceed quite rapidly and the process could be relatively less costly with the pilot plant. For these reasons it is recommended that the process be scaled-up by a contractor.

The pilot-phase cost will be less than 0.01% of the projected commercial deployment costs. Although the recommended bench-scale effort would have an important bearing on the pilot-plant design and on the projected yields from various feedstocks, its impact on the pilot-plant cost would be relatively low.

SECTION 4

PYROLYSIS

BACKGROUND

Pyrolysis involves the heating of organic material without combustion until it decomposes to form gases, liquids, and/or char. Considering that cellulosic organic material includes a broad spectrum of possible chemical compounds, it is not surprising that its decomposition results in many different pyrolysis products. There are, however, three major pyrolysis reactions which take place simultaneously at different rates. The relative reaction rates are much affected by temperature. As shown in Figure 1, at relatively low temperatures (e.g., 200-300°C), the dehydration reaction to form primarily char and water predominates. This reaction takes place relatively slowly and has been utilized for centuries to produce charcoal. At higher temperatures, the cleavage of the large organic molecules, such as cellulose, into smaller molecules creates relatively large amounts of oxygenated tars.(5) At temperatures above 700°C, the predominant reaction is to form gaseous hydrocarbons, low-molecular-weight oxygenated hydrocarbons, carbon monoxide, and carbon dioxide. This gasification reaction produces relatively reactive hydrocarbon pyrolysis products which will further react to form aromatic tars and eventually char if allowed to remain at the pyrolysis temperature several seconds. The gasification reaction to form the desirable hydrocarbons will not take place if the heating rate of the organic material is so slow as to allow the char-forming, dehydration reaction to occur first.

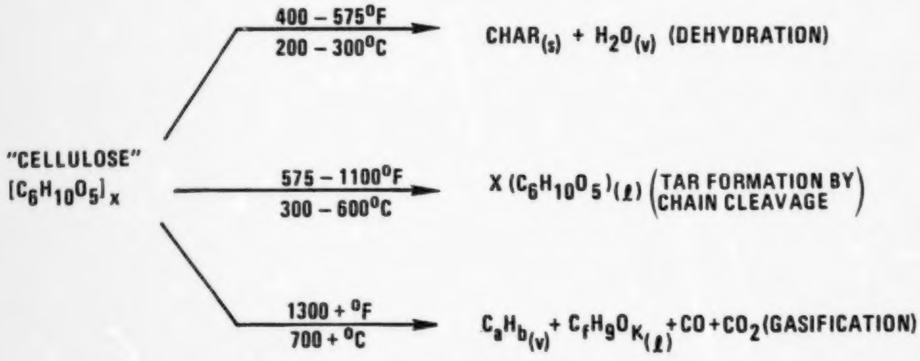

400 – 575°F
200 – 300°C
CHAR(s) + H2O(v) (DEHYDRATION)
"CELLULOSE"
[C6H10O5]x
575 – 1100°F
300 – 600°C
X (C6H10O5)(ℓ) (TAR FORMATION BY CHAIN CLEAVAGE)
1300 + °F
700 + °C
CaHb(v) + CfHgOK(ℓ) + CO + CO2 (GASIFICATION)

Figure 1. Competing Pyrolysis Reactions.

Prior to the pyrolysis work performed at NWC, there were some intriguing organic pyrolysis results reported in the literature which indicated the potential for the high-temperature pyrolysis reaction to make gaseous, unsaturated hydrocarbon products. Very slow pyrolysis of relatively large pieces of municipal trash in an updraft vertical shaft reactor was reported to produce gases containing only about 1/2% by volume ethylene.(6) This type of pyrolysis apparently did not favor the desired decomposition reactions, and the introduction of combustion air at the bottom of the shaft probably served to combust not only char, but some of the hydrocarbons formed as well.

More favorable results were reported for the batch pyrolysis of relatively wet municipal trash organics. In these experiments, a retort measuring 46 centimeters in diameter and 66 centimeters long was loaded with about 36 kilograms of trash containing 43% moisture by weight. The retort was then electrically heated for 6 to 12 hours. The pyrolysis apparently proceeded from the material near the walls of the retort slowly toward the center of the cylindrically shaped mass of trash. Heating the trash in this manner would cause the moisture to turn to steam at about 100°C and then to pass out through the hotter pyrolysis zones. In effect, the pyrolysis gases were diluted by the steam at an average ratio of 0.9 kilogram steam per kilogram of dry, ash-free organic. The pyrolysis gases were free to leave the hot decomposition zone as soon as they were formed. This dilution effect, along with the short residence time of the product gases in the reactor, apparently contributed to the relatively high 10%-by-weight conversion to hydrocarbons other than methane (C_2 + hydrocarbons).(7)

In experiments more closely approaching continuous operation, a very small quantity (1 to 5 grams) of organic material was placed in a preheated reactor and allowed to pyrolyze over a 2- to 3-minute period. The gases were free to leave the hot pyrolysis zone as soon as they were formed, and they had an estimated residence time of less than 1 second. When black pine bark was used, it was noted that the production of ethylene was increased by one-third if wet bark (44% moisture) was used instead of dry bark (10% moisture). An overall conversion of 10% by weight to C_2 + hydrocarbons was reported for the wet bark. Speculation was that work with a continuous pyrolysis reactor was needed.(8)

Using MSW shredded to less than 1.25 centimeters (1/2 inch) in a continuous laboratory-sized pyrolysis reactor produced significant quantities of ethylene (∿4% by weight) at about 800°C. The wastes had an equivalent of 24% moisture by weight.(9)

With a plastics-rich MSW feedstock in which the inorganics and half of the paper had been removed, yields of up to 27% by weight ethylene, propylene, butylene, etc., were reported using an implied residence time of 0.1 to 0.6 second in an entrained bed reactor.(10) (11) These exceptionally high yields of hydrocarbons were at least in part due to the apparently high plastics content, since plastics like polyethylene can be pyrolyzed to yield as high as 78% by weight ethylene, propylene, butylene, etc.(12) Hydrocarbon oils can also be "steam cracked" or pyrolyzed to produce from 61% to 78% by weight light hydrocarbons (acetylene through xylene) from crude oil and naphtha respectively.(13) Thus, it appears that the relative yields of hydrocarbons suitable for making gasoline by this proposed process depends on the initial hydrocarbon content of the feedstock. For example, the pyrolysis of resinous pine sawdust would be expected to have significantly higher yields of the desired olefins than from a non-oily feedstock such as cornstalks. A correlation between the heat of combustion of the feedstock and the yield of desired olefins would be expected, since the hydrocarbon-containing feedstocks will have a higher heat of combustion on a weight basis.

With an extremely high heating rate provided by an intense 0.5 millisecond xenon flash, 30%-by-weight volatile organics, no tar, and 1% char were reported from cellulose.(14) A mass balance calculated for the overall reported pyrolysis results revealed that the "volatiles" had virtually no oxygen and had a hydrogen-to-carbon ratio of 1.38. Assuming that the "volatiles" were a mixture of ethylene and acetylene, a yield of 9% ethylene and 21%-by-weight acetylene was calculated.

EXPERIMENTAL

Pyrolysis Feed

The solid waste feed chosen for the pyrolysis evaluation was ECO II$^{\text{TM}}$ fuel produced by Combustion Equipment Associates, New York. This material was processed from Connecticut municipal waste by coarse shredding, organic fraction recovery, chemical treating, and subsequent ball milling. This resulted in a very fine, nonfibrous, free-flowing material having an average particle size of about 250 μm and a particle distribution as shown in Figure 2. This material was developed for use as a low-sulfur-containing coal substitute at a price of about \$2.11/GJ (\$2/MBtu) in 1975. The company supplied a chemical analysis on a composite sample of the ten 20.8-decaliter (55-gallon) drums shipped to NWC

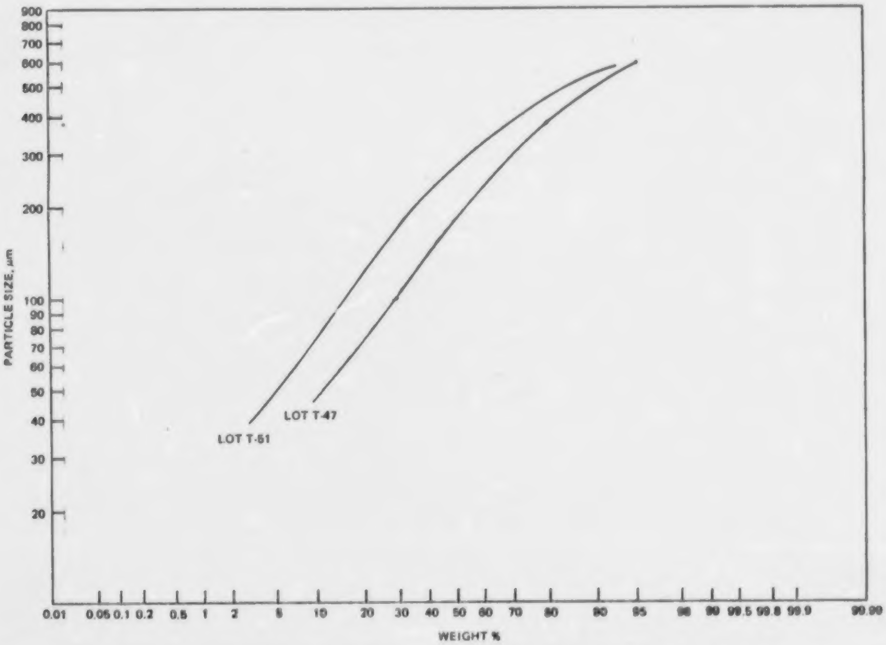


Figure 2. Particle Size Distribution, ECO II Fuel.

for the program. An independent analysis was run on two of the drums to determine drum-to-drum variability, since the material shipped was the product of a process variable study. The results of those analyses are shown in Table 1. Other data included in the table are those previously reported for MSW, for cellulose containing 12% ash, and for computer cards. The latter are of interest because the pieces punched out of the cards are very uniform and would be useful to evaluate the effect of composition and feed particle size on pyrolysis parameters.

The ECO II ash fusion temperatures were reported to be between 1096 and 1196°C which was well in excess of the 700 to 900°C used for pyrolysis in the program. The most noticeable difference between the ECO II fuel and cellulose containing a hypothetical 12% ash is that the ECO II has about 5 to 10% more carbon and 10% less oxygen. This difference may be due to the presence of free carbon in the ECO II fuel. During the manufacture of ECO II, the inorganic fraction of the trash is first removed. Then, the organic fraction is treated with a inorganic proprietary chemical to embrittle the cellulosic materials. The embrittled material is then ball-milled at elevated temperatures (93 to 204°C).(15) The effect of the treatment is apparently to increase the carbon content, probably by a char-forming (dehydration) mechanism, as well as to increase the sulfur and chlorine content. Much of the sulfur is probably present as sulfates since the resultant pyrolysis gases did not appear to have a very high hydrogen sulfide content. Much of the differences in heat of combustion of the ECO II values can be explained by correcting for ash content.

Gas Chromatograph

Gas analysis for the project required a very broad range of capability; i.e., from hydrogen and the permanent gases to hydrocarbon species up through pentane. The gas chromatograph system chosen for this application was the AGC-111H (Spec. 1511) manufactured by Carle Instruments, Inc., Fullerton, CA. This is an isothermal gas chromatograph consisting of four absorption columns in series interconnected by a complex valving arrangement. Helium is the carrier gas into which the sample is injected either from a 1-milliliter syringe directly or from the 1-milliliter sample valve. The sample is then swept through the columns by the helium carrier gas. As the sample passes through the columns, certain compounds are selectively absorbed by the column material to effect their separation.

Hydrogen is swept through the columns in about 3 minutes, at which time it passes into the palladium hydrogen transfer tube. The hydrogen diffuses through the palladium tube, leaving the helium carrier gas behind. A nitrogen carrier gas then sweeps the hydrogen through a thermal conductivity cell where the hydrogen is easily detected by the change in thermal conductivity of the gas. This method of hydrogen analysis is advantageous because the thermal conductivity of hydrogen is very close to that of helium whereas it is easily detected in nitrogen.

In the original configuration of the chromatograph, after the hydrogen was eluted and detected, all of the columns were isolated and then accessed one at

TABLE 1. PYROLYSIS FEED ANALYSIS

Sample	Weight % moisture	Weight %, dry basis							Particle size, average, µm	Dry basis heat of combustion HHV, cal/g (Btu/lb)
		Ash	C	H	O	N	S	Cl		
ECO II* (composite NWC)	3.82	11.87	. . .	. . .	. . .	. . .	0.73	0.70	. . .	4,754 (8,558)
ECO II** (drum T-47)	1.69	12.46	45.50	6.20	34.22	0.27	0.98	0.37	188	4,726 (8,507)
ECO II** (drum T-51)	0.91	9.73	49.64	6.40	32.38	0.22	1.04	0.59	270	5,306 (9,550)
Altoona, PA#	43.3	12.0	47.6	6.0	32.9	1.2	0.3	. . .	. . .	4,748 (8,546)
Dry cellulose + 12% ash	0	12.0	39.11	5.4	43.45	. . .	. . .	. . .	. . .	3,677 (6,618)
IBM computer cards**	3.8	0.68	43.21	6.46	49.45	0.10	0.023	0.080	. . .	3,920 (7,056)

*Commercial Testing and Engineering Company, Chicago, Ill.

**Truesdail Laboratories, Los Angeles, Calif.

Sanner, W. S., et al. *Conversion of Municipal and Industrial Refuse into Useful Materials by Pyrolysis.* August 1970, p. 3. (BuMines Report 7428.)

a time. The squalane-noctane/Porasil C columns contained the trapped propanes (C_3's), butanes (C_4's), n-pentane, and isopentane. The Porapak S column contained carbon dioxide, ethylene, ethane, and acetylene. The molecular sieve (13X) column contained the oxygen, nitrogen, methane, and carbon monoxide. The complete analysis including backflushing required only 30 minutes.

Unfortunately, although the ethane and the acetylene were both separated from the other constituents, they were not separated from each other. This resulted in a single elution peak for the two compounds. After consultation with the manufacturer, the original Porapak S column was replaced with a Porapak N column. This alteration resulted in good acetylene and ethane separation, but also in a merger of the carbon dioxide and ethylene elution peaks, which was very undesirable. Further consultation with the manufacturer resulted in his sending a specially prepared column of 50% Porapak Q and 50% Porapak N to replace the original Porapak S column. This resulted in the excellent C_2 separation shown in Figure 3. The valves were controlled by a programmed timer.

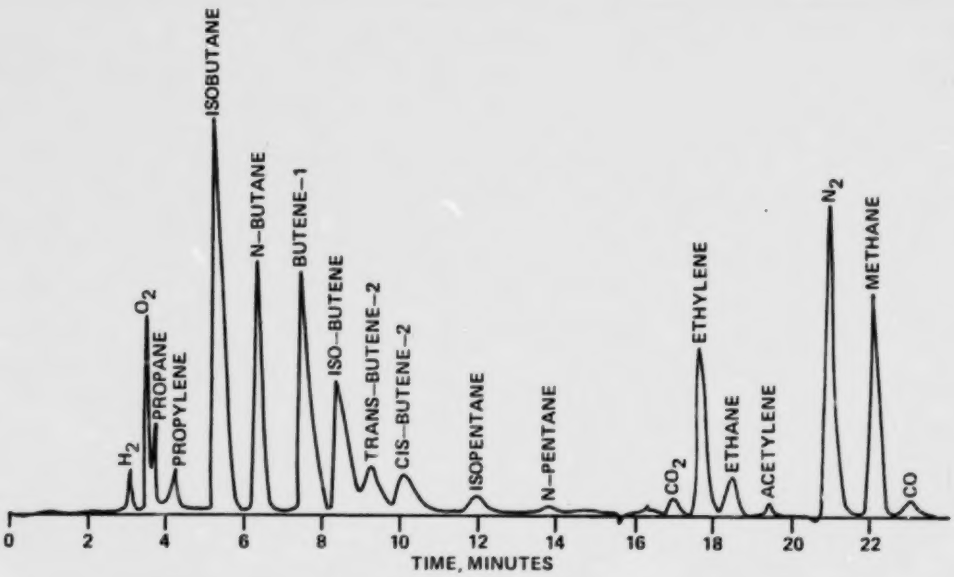


Figure 3. Gas Chromatograph Calibration Example.

The millivolt signal from the gas chromatograph detector was input to a Houston Instrument's Omniscribe Model 7302 recorder. This recorder plots the elution signals as well as the electronically integrated signal. The integrated signals are then used with calibration factors to calculate the gas composition.

Calibration of the elution times and response factors was carried out using several off-the-shelf gas mixtures sold by Phillips Petroleum. Unfortunately, a minimum of four analyses was required for a complete calibration check. A custom 20-component gas mixture was obtained which allowed the elution calibration with one analysis (30 minutes). The component concentrations of the gas mixture were chosen so that the calibration run might proceed without the need to manually change the attenuation during the run.

The thermal response values used to convert the gas chromatograph data to volume percentages for the first 40 pyrolysis runs were obtained with standards from Phillips Petroleum. In 1959,(16) and again in 1967,(17) workers at Esso Research and Engineering Company, Linden, NJ, reported thermal response factors for a large number of compounds. They further established that the relative response factors were independent of the thermal detection method (thermistors vs. hot wire), temperature, concentration, and carrier gas flow. It was decided to utilize these reported thermal response factors for this program rather than to expend more effort in obtaining thermal response factors from calibration gas mixtures. This decision resulted in some minor changes to the values of the response factors, but did not significantly change previously reported data.

Mass and Energy Balance Computer Program for Pyrolysis

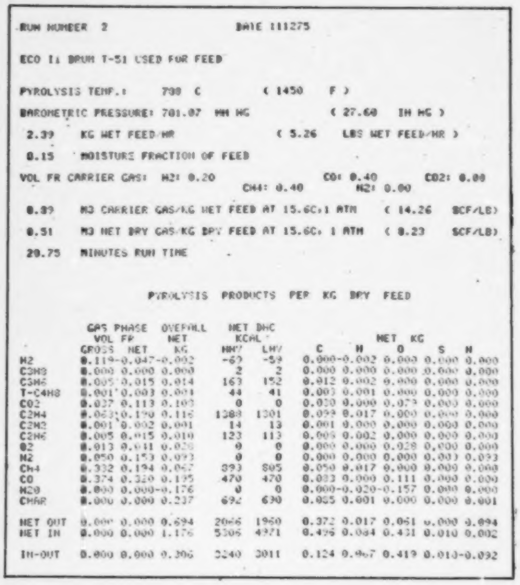
The basic language program (Hewlett-Packard HP-9830 computer) to generate the pyrolysis mass and energy balances was written and debugged. This program was deemed necessary to help identify systemic errors and/or impossible results as well as to provide information for optimization and eventual scale-up. The program asked for the run number, date, pyrolysis temperature, raw gas chromatograph data, carrier gas composition and flow rates, barometric pressure, line pressure, product and feed weights, and moisture fraction of feed. The program then printed out on an 8 1/2- x 11-inch summary sheet: the run number and date, the pyrolysis conditions, the carrier gas composition, the gross product gas composition, the net product gas composition (without the carrier gas), the itemized pounds of net product per pound of dry feed, the heat of combustion of each product per pound of dry organic feed, and an elemental balance. Although these calculations are all straightforward, they would have been tedious to hand calculate for each run.

The program generates the mass and energy balances through the following sequence of calculations:

1. The composition of the gross pyrolysis gases by volume.
2. The weight of each gross pyrolysis gas specie per unit weight of dry feed from step 1.
3. The weight of each carrier gas specie per unit weight of dry feed.
4. The net weight of pyrolysis products by subtracting step 3 results from step 2 results.
5. The heating value of each product by multiplying the weight by its heat of combustion (both higher and lower heating values are calculated).
6. The elemental weights of each product by multiplying each product weight by its weight fraction of that element.
7. Mass and energy balances with steps 4, 5, and 6.

In addition, the feed rates and the net volume of pyrolysis gas per unit weight of dry feed are calculated in both U.S. and metric units.

Approximately 3 minutes are required to enter the raw data and to obtain the Pyrolysis Summary Sheet, a sample of which is shown in Figure 4.



```
RUN NUMBER  2                    DATE 111275

ECO I; DRUM T-51 USED FOR FEED

PYROLYSIS TEMP.:    788  C           ( 1450    F )

BAROMETRIC PRESSURE: 701.07  MM HG              ( 27.60   IN HG )

 2.39    KG WET FEED/HR                ( 5.26    LBS WET FEED/HR )

 0.15    MOISTURE FRACTION OF FEED

VOL FR CARRIER GAS:  H2: 0.20               CO: 0.40        CO2: 0.00
                                 CH4: 0.40       N2: 0.00

 0.89    M3 CARRIER GAS/KG WET FEED AT 15.6C, 1 ATM    ( 14.26   SCF/LB)

 0.51    M3 NET DRY GAS/KG DRY FEED AT 15.6C, 1 ATM    ( 8.23    SCF/LB)

 20.75   MINUTES RUN TIME


                PYROLYSIS  PRODUCTS  PER  KG  DRY  FEED


          GAS PHASE  OVERALL   NET DHC
           VOL FR     NET      KCAL                 NET  KG
          GROSS  NET   KG      HHV   LHV     C     H     O     S     N
H2        0.119-0.047-0.002    -69   -59   0.000-0.002 0.000 0.000 0.000
C3H8      0.000 0.000 0.000      2     2   0.000 0.000 0.000 0.000 0.000
C3H6      0.005 0.015 0.014    163   152   0.012 0.002 0.000 0.000 0.000
T-C4H8    0.001 0.003 0.004     44    41   0.003 0.001 0.000 0.000 0.000
CO2       0.027 0.113 0.103      0     0   0.030 0.000 0.073 0.000 0.000
C2H4      0.063 0.190 0.116   1388  1301   0.099 0.017 0.000 0.000 0.000
C2H2      0.001 0.002 0.001     14    13   0.001 0.000 0.000 0.000 0.000
C2H6      0.005 0.015 0.010    123   113   0.008 0.002 0.000 0.000 0.000
O2        0.013 0.041 0.028      0     0   0.000 0.000 0.028 0.000 0.000
N2        0.050 0.153 0.093      0     0   0.000 0.000 0.000 0.000 0.093
CH4       0.332 0.194 0.067    893   805   0.050 0.017 0.000 0.000 0.000
CO        0.374 0.320 0.195    470   470   0.083 0.000 0.111 0.000 0.000
H2O       0.000 0.000-0.176      0     0   0.000-0.020-0.157 0.000 0.000
CHAR      0.000 0.000 0.237    692   630   0.035 0.001 0.000 0.000 0.001

NET OUT   0.000 0.000 0.694   2066  1950   0.372 0.017 0.061 0.000 0.094
NET IN    0.000 0.000 1.176   5306  4971   0.496 0.084 0.431 0.010 0.002

IN-OUT    0.000 0.000 0.306   3240  3011   0.124 0.067 0.419 0.010-0.092
```

Figure 4. Pyrolysis Summary Sheet.

Orifice Meter

It was originally intended to measure noncondensable gas flow only with an orifice meter. However, to know the quantitative flow rate through an orifice meter, the gas composition must be known. Although the gas composition could be analyzed, this information would not be available during a pyrolysis run. Therefore, a "natural gas" positive displacement meter was added to provide a quantitative volume flow-measuring capability. During the course of checking the flow meters against each other, it was realized that many of the factors governing the orifice meter measurements were relatively constant in this case. Furthermore, the orifice meter theory indicated that a positive displacement meter in series with the orifice meter would allow the average molecular weight, and therefore the true mass flow rate, to be calculated as shown below.

The equation(18) governing an orifice meter with a small pressure drop is:

$$\dot{w} = CYA_2\sqrt{\frac{2gc\ (\Delta P)\rho_1}{1 - \beta^4}}$$

where

$\dot{w}$ = mass flow rate

C = orifice discharge coefficient

A_2 = orifice diameter

gc = acceleration of gravity

β = ratio of orifice diameter to pipe diameter

ΔP = pressure drop across the orifice

ρ_1 = upstream gas density

Y = expansion factor; for subsonic flow

$$Y = 1 - \left(\frac{1 - r}{k}\right) (0.41 + 0.35\beta^4)$$

where

r = ratio of downstream to upstream pressure

k = specific heat ratio

Y is near unity (0.998) for a 1.22-centimeter (0.483-inch) orifice in a 2.51-centimeter (0.990-inch) diameter pipe with gas having a specific heat ratio of 1.41 and at a 4.8-centimeter (1.89-inch) water pressure differential; therefore, changes in K may be neglected for all purposes. This approach of Y to unity is primarily due to the near-unity value of r (0.995), caused by the low-pressure drop.

The discharge coefficient of an orifice is a complex function of β and the gas viscosity, density, and velocity (Reynolds number). However, at relatively high flow rates, the discharge coefficient becomes relatively constant. For the case given above, the discharge coefficient was experimentally determined to vary only between 0.631 and 0.639 for air flow rates of 0.042 to 0.14 m^3/min (1.5-5 ft^3/min). This coefficient may be assumed to be constant with very little error over this flow regime ($C = 0.634$, $\sigma_c = 0.003$).

If the ideal gas law ($PV = nRT$) is assumed and the volumetric flow rate is known, then the equations may be algebraically combined and rearranged to give

$$M = \frac{\Delta H}{V_1^2} \left(\frac{\rho_{H_2O}\ C^2 A_2^2\ 2gc\ RT_1}{(1 - \beta^4) P_1} \right)$$

where

M = average molecular weight of the gases

ΔH = pressure difference

ρ_{H_2O} = density of water

R = universal gas constant

V_1 = volumetric flow rate

P_1 = absolute pressure

T_1 = absolute temperature

For a specific orifice at a constant temperature and pressure, this equation can be expressed as

$$M = K \Delta H / V_1^2$$

where K is a constant and the orifice discharge coefficient and expansion factor are assumed constant.

The system was calibrated with air (molecular weight 28.97); then bottled methane (CP) was run through the system. A molecular weight of 15.6 was calculated for the methane gas. Pure methane has a molecular weight of 16.0, so the molecular weight was measured with only a 2.5% error. Since some of the error is thought to be systemic, it is anticipated that the molecular weight meter could differentiate between gases having very similar molecular weights, such as ethane and ethylene. This molecular-weight-measuring capability could aid in the on-line identification of unknown gas streams or in the control of processes where the molecular weight of the synthesis gas must be accurately maintained, such as in methanol or ammonia manufacture. The "molecular weight" meter is very simple; and, for a laboratory setup, one could use a wet test meter or a bubble meter to measure small gas flows.

Feeding System

The pyrolysis feed system consisted of a VibraScrew™ feeder having a screw auger 2.540 centimeters (1 inch) in diameter. This unit had a variable speed transmission to vary the feed flow rate. At the end of the screw auger, a small metal bar was added to help dislodge the feed from the auger. The carrier gas stream was split into two portions: one part fluidized the feed by blowing it off the auger, and the other part served to pump the material toward the pyrolysis reactor by passing through an ejector nozzle. The feed was then conveyed to the pyrolysis reactor in a 1.6-centimeter ID tube (1/2-inch pipe) for the first 47 runs. The feed transfer tube was later changed to a 0.6-centimeter (1/4-inch) rubber hose to reduce the required amount of carrier gas and to aid in the occasional unplugging of the system. The small-diameter hose plugged more readily; however, by shortening the feed transfer tube to about 25 centimeters, reliable feeding could be accomplished even with a 1.25-centimeter (1/2-inch) diameter tube. The positioning of the feeder above the steam ejector so that the gravity could help in the transfer was also helpful. The solids feeding system was a source of minor problems (e.g., plugging), but this would probably be less of a problem in a scaled-up system using similarly sized feed particles.

Carrier Gas Mixtures

The composition of the carrier gas used to blow the feed into the pyrolysis reactor was one of the variables investigated early in this program. To accomplish this, rather than purchase gas mixtures, it was decided to purchase bottles of pure methane, hydrogen, carbon monoxide, and carbon dioxide. The pure gases were then used to make gas mixtures as needed. Instead of metering the individual gases at the time of use, they were premixed and stored. This method ensured that the gas composition would be constant during the pyrolysis runs so that accurate mass balances could be made. The gas mixing equipment consisted of the four bottles of pure gases manifolded to two storage bottles. Check valves were installed to protect the purity of the individual gases. A precision Heise gauge was used to indicate the pressure of the gas mixture. Each bottle of pure gas had a small pressure gauge and needle valve so that the bottle pressure could be checked independently of the gas mixing operation. This plumbing arrangement was constructed from parts purchased from Linde Gas Company, Los Angeles.

The first attempt to use this equipment was to make a mixture of 20% hydrogen, 40% methane, and 40% carbon monoxide. To the methane in its storage bottle sufficient carbon monoxide was added to double the initial pressure. Hydrogen was then added until the correct final pressure was attained (assuming ideal gas behavior). This mixture was allowed to sit for 2 hours before it was used in pyrolysis run 2. Based on the initial gas flow rates measured and several gas chromatograph analyses, it was apparent that the gas mixture was far from uniform. The very light hydrogen had stratified on top of the other gases when it was added to the storage bottle so that initially the gas mixture was *very* rich in hydrogen and eventually *extremely* lean.

A second gas mixture was made using the residual gas mixture in which the hydrogen was added first, followed by the heavier methane and then carbon monoxide. The gas mixture composition was to have been the same as before. After 3 days of vertical storage at ambient room temperature, the gas mixture was analyzed. After a total of 18 days, it was used for the carrier gas in pyrolysis run 5. The gas mixture was sampled three times during the run with analyses as presented in Table 2. The presence of trace amounts of nitrogen and oxygen was probably due to sampling technique.

The ability to easily make fairly precise gas mixtures had been demonstrated, as well as the requirement for the mixture to stand several days to equilibrate. After 18 days of storage the gases appeared to have been uniformly mixed by gas diffusion. After 3 days of storage, the uniformity of the mixtures was thought to be adequate for this program, since it was planned to sample the gas mixture while it was being used.

One interesting anomaly was noted during this experimentation. The pressure of the gas mixture decreased with time, but appeared to eventually stabilize. This decrease in pressure is thought not to be due to leakage, but rather to nonidealities of the gas mixture. The gas mixture appears to exert less pressure than the same amounts of individual gases at identical conditions. This pressure shrinkage was on the order of 7 to 10% of the initial pressure. The stabilization of the mixture pressure appeared to be indicative of the mixture's uniformity.

TABLE 2. GAS MIXTURE STUDY RESULTS

Gas	Volume Fraction					
	Goal	After 3 days	After 18 days			Average after 18 days
			Beginning	Middle	End	
H_2	0.20	0.190	0.169	0.170	0.156	$0.165\ ^{+0.005}_{-0.009}$
CH_4	0.40	0.415	0.433	0.435	0.438	$0.435\ ^{+0.003}_{-0.002}$
CO	0.40	0.393	0.394	0.393	0.394	$0.394\ ^{+0.000}_{-0.001}$
N_2	....	0.002	0.004	0.002	0.008	
O_2	....	.....	.....	.....	0.004	

Initial Fluidized Bed Pyrolysis Reactor

The initial approach to the pyrolysis reactor was an electrically heated fluidized bed as shown in Figure 5. The fluidized bed was in a stainless steel tube having inside dimensions of 9.5 centimeters in diameter and 71 centimeters long. The solid feed and carrier gas were introduced near the bottom of the bed. The pyrolysis gases were to exit at the top of the reactor. During the initial shakedown pyrolysis runs, it became apparent that the reactor was only heating the pyrolysis gases to about 500°C (∿925°F)) in spite of the 800°C (∿ 1,475°F) temperature of the fluidized char bed.

Walls of loosely stacked insulating fire brick were built around the 38-centimeter diameter by 38 centimeter-high cyclone separator in hopes of increasing the residence time at high temperatures to increase the degree of pyrolysis. A propane burner in the shape of a ring was soon added to the bottom of the cyclone to maintain the pyrolysis temperature in the cyclone. The propane heating of the cyclone was manually controlled relatively easily.

At this point, an excessive pressure drop had developed across the reactor. Disassembly of the reactor revealed that the larger, heavier pieces of feed had been accumulating at the bottom of the reactor, and had caused the gases to channel up through the accumulated nonfluidized debris. This lack of a fluidized bed had been responsible for the lack of anticipated heat transfer. It

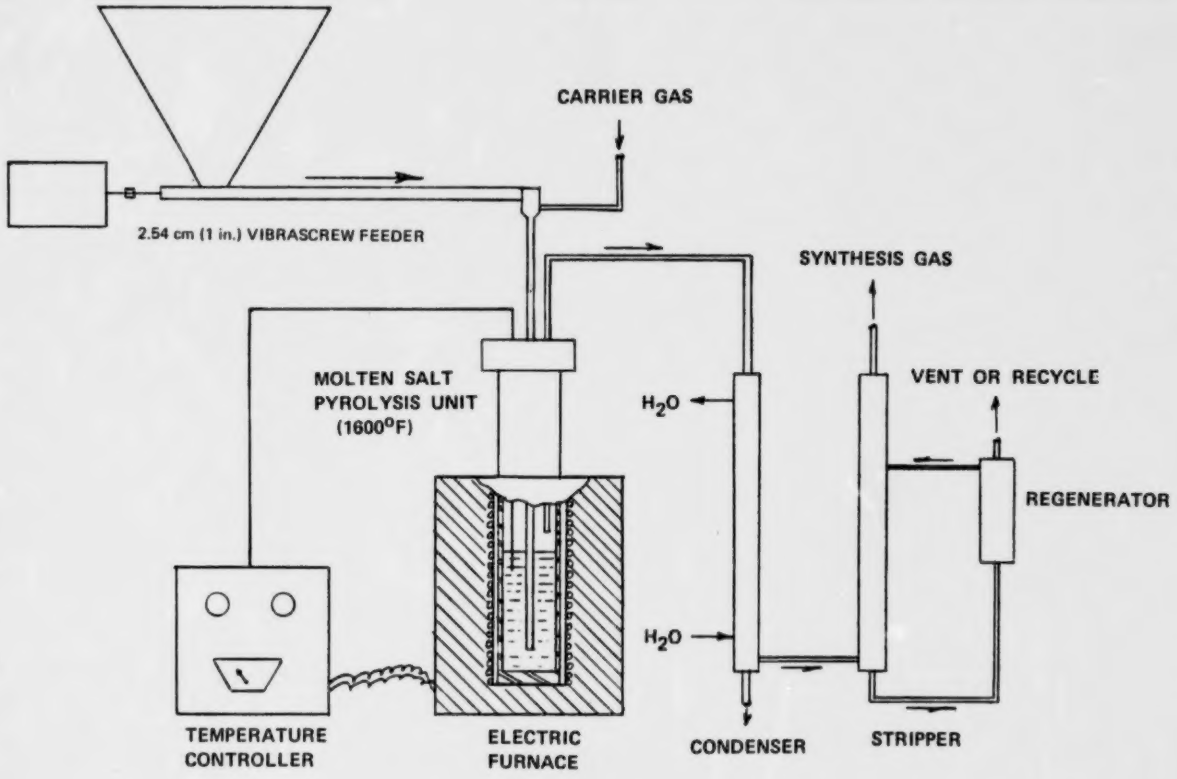

CARRIER GAS
2.54 cm (1 in.) VIBRASCREW FEEDER
SYNTHESIS GAS
MOLTEN SALT
PYROLYSIS UNIT
(1600°F)
H_2O
VENT OR RECYCLE
REGENERATOR
H_2O
TEMPERATURE
CONTROLLER
ELECTRIC
FURNACE
CONDENSER
STRIPPER

Figure 5. Initial Pyrolysis Schematic.

was obvious that the reactor would need to be cooled and disassembled after short periods of operation to remove the heavy debris. The cleaning out of the reactor several times a day was contrary to the program goal of successfully mating the pyrolysis and the polymerization units. It was also noted that the heavy debris would accumulate in the reactor regardless of the heat transfer medium (i.e., char, sand, molten metal, or salts). In the interest of the program goals, it was decided that the fluidized bed approach would be set aside and a variation of the entrained reactor investigated. The electrically heated furnace and reactor were also set to one side.

"Long-Residence-Time" Reactor

The feed transport tube was modified to connect the bottom of the feeding system to the cyclone separator. One experimental run was sufficient to show that additional heat transfer into the feed and pyrolysis products was necessary. A length of 1.9-centimeter (3/4-inch) stainless steel tubing was obtained and bent once around the cylindrical portion of the cyclone so as to fit inside of the insulating bricks built around the cyclone. This setup was tried with the carrier gases sweeping the feed particles once around the cyclone before they entered the cyclone. Thermocouples on the outside wall of the heated tubing indicated temperatures of about 700°C (∿ 1,300°F) when the flue gas temperature was at about 800°C (∿ 1,450°F). A residence time of about 0.2 second in the preheating tube was calculated. An additional length of tube was then added so that the feed would pass twice around the cyclone before entering the cyclone, as shown in Figure 6. The total length of heated tubing upstream of the cyclone was then 2.8 meters (9.2 feet). The wall temperature of the tubing near the entrance of the cyclone was basically the ambient flue gas temperature, whereas slightly lower wall temperatures were seen at the beginning of the heated tubing where the cold feed entered. Estimated residence times were about 0.3 to 0.4 second in the 3/4-inch tubing and 5 to 10 seconds in the cyclone separator. This pyrolysis reactor, as seen in Figure 6, was used for runs 1 through 20. The initial data were confounded by at least one of several complications encountered during each run; i.e., loss of carrier gas up through the feed hopper due to the pressure backing up during plugging, variable carrier gas composition, leaks, and in one case unknown moisture content of the feed.

Figure 7 is a typical gas chromatograph curve made with the pyrolysis gases from run 1. This run utilized ECO II fuel as feed and methane as the carrier gas such that the gross pyrolysis gases should have contained about 67% carrier gas and 33% pyrolysis gases. The computer calculations showed that either methane carrier gas was consumed in the pyrolysis reaction or, more probably, some of the carrier gas escaped up through the feed hopper. As shown in Table 3, this run at 760°C (1400°F) produced at least 12 grams of usable hydrocarbons (C_2+) per 100 grams of dry feed in the following amounts: 0.1 gram acetylene, 8.2 grams ethylene, 1 gram ethane, 1.8 grams propylene, 0.4 gram propane, and 0.5 gram trans-butene-2. These amounts of usable hydrocarbons are based on the original moisture content of 0.1% of the feed, although the feed had been exposed to about a 50% humidity environment. The probable higher moisture content of the feed would increase these hydrocarbon production numbers proportionately. There were 24 grams of char produced per 100 grams of dry feed, of which about 10 grams was ash based on the elemental analysis. The run time was 43.5 minutes, and 2779 grams of feed were pyrolyzed.

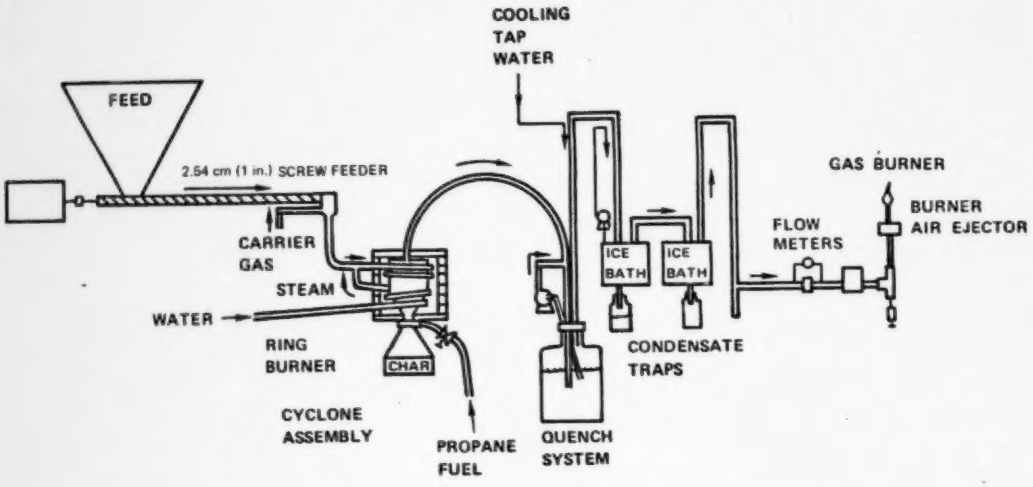

COOLING
TAP
WATER
FEED
2.54 cm (1 in.) SCREW FEEDER
CARRIER
GAS
STEAM
WATER
RING
BURNER
CHAR
CYCLONE
ASSEMBLY
PROPANE
FUEL
QUENCH
SYSTEM
ICE
BATH
ICE
BATH
CONDENSATE
TRAPS
FLOW
METERS
GAS BURNER
BURNER
AIR EJECTOR

Figure 6. Long-Residence-Time Pyrolysis Reactor.

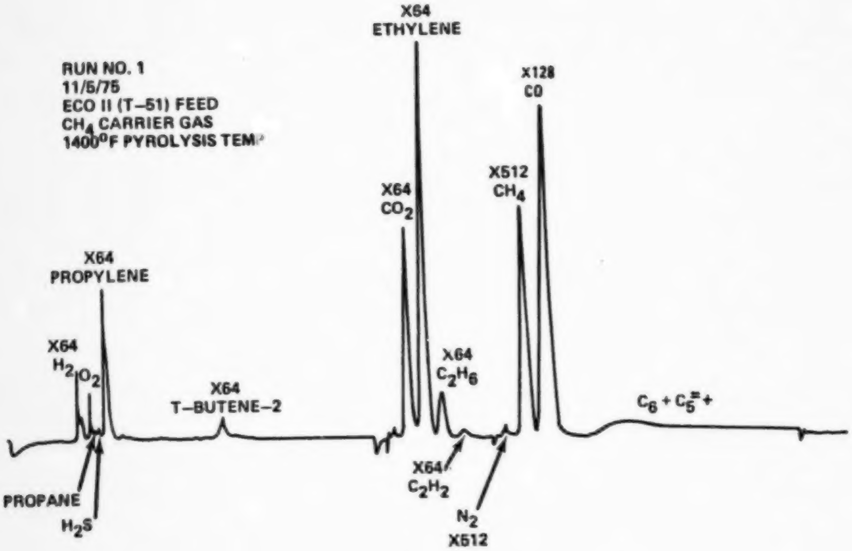


Figure 7. Gas Chromatograph Output for Run 1.

TABLE 3. PYROLYSIS SUMMARY FOR THE LONG-RESIDENCE-TIME REACTOR

Run	Moisture, %	Wet feed rate, kg/hr	Pyrolysis temp, °C	Carrier gas					Steam		Residence time, sec	g dry feed/m^3 total gases	Grams net product/100 grams dry feed											
				Mole %				m^3/kg of dry feed*	m^3/kg of dry feed*	kg/kg dry feed			CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_4H_8	$C_5^=$+ C_6+	H_2	CO	CO_2	Char	C_2+
				H_2	CH_4	CO	CO_2																	
1	1*	3.83	760	0	100	0	0	0.55	0	0.01	N/A	302	-2.3†	0.1	8.2	1.0	1.8	0.5	**	0.3	24.1	6.7	24.0	12.0
2	15	2.39	790	#	#	#	0	0.89	0	0.18	N/A	175	6.7**	0.1	11.6	1.0	1.4	0.4	**	-0.2†	19.5†	10.8	23.7	15.0
3	10	3.43	815	0	0	100	0	0.39	0	0.11	N/A	297	6.6	0.2	7.4	0.6	0.7	0.3	**	0.6	18.7†	8.6	15.7	9.3
4ζ	10	3.98	850	0	0	100	0	0.25	0	0.11	N/A	461	4.1	0.2	4.3	0.2	0.2	0.1	**	0.4	9.6†	4.1	15.0	5.1
5	10	3.05	815	16	44	40	0	0.30	0	0.11	N/A	330	8.8†	0.2	7.8	0.6	0.5	~0.1	**	-0.2†	25.9†	8.8	18.6	9.3
6	10	3.60	732	0	100	0	0	0.78	0	0.11	N/A	300	-18.0	0.1	5.7	1.1	2.3	1.3	3.6	0.5	19.4	5.4	20.5	14.2
14	1	4.22	732	0	0	0	100	0.13	0.88	0.67	4.3	175	3.6	0.1	5.7	0.8	1.7	0.7	2.1	0.4	18.2	4.8†	12.2	11.2
15	1	3.86	732	0	0	0	100	0.13	0.96	0.74	3.9	148	7.0	0.3	5.9	0.8	1.4	0.7	1.8	0.6	20.6	4.3†	12.3	11.0
16	1	4.08	788	0	0	0	100	0.16	0.91	0.70	3.7	147	5.2	0.3	7.3	0.6	1.0	0.4	3.2	0.8	23.0	0.3†	12.2	12.9
17	1	3.91	682	0	0	0	100	0.18	0.95	0.65	4.6	176	3.4	0.2	5.2	0.9	2.2	1.3	3.4	0.4	18.8	-4.4†	18.9	13.3
18	1	3.85	552	0	0	0	100	0.17	0.96	0.74	6.3	237	0.8	0	1.5	0.3	0.7	0.3	1.6	0.1	7.0	-0.7†	27.7	4.5
19	1	1.71	860	0	0	0	100	0.40	2.16	1.13	5.8	96	5.2	0.6	6.9	0.3	0.3	0.1	4.0	1.3	21.8	-23.3†	4.6	12.4
20	1	3.12	716	19	42	39	0	0.37	1.19	0.91	4.6	138	-1.0†	0.2	5.0	0.9	1.5	0.7	1.7	0.2†	10.4†	7.4	7.0	10.1

*At 15.6 °C, 101 kPa (14.7 psi).

**Data not meaningful due to use of organic solvents in the quench system.

#This carrier gas was poorly mixed 20% H_2, 40% CO, and 40% CH_4.

†These data were not reliable, since this gas was used as part of the carrier gases.

ζRun 4 is suspected to have a leak of pyrolysis gases, since the gaseous product weights were all very low.

Other carrier gases employed initially were methane, carbon monoxide, and mixtures of hydrogen, methane, and carbon monoxide. Pyrolysis temperatures varied from 760 to 850°C (1400 to 1560°F). Carrier gas flow rates varied from 0.25 to 0.89 m^3/kg dry feed, and moisture contents were varied from 1 to 15%. There were definite changes in the net pyrolysis gas composition and conversions of feed to usable hydrocarbons. It appears that pyrolysis temperatures above 800°C (1450°F) resulted in an undesirable and rapid decline of the propylene and butylene production and caused an overall decline in the usable hydrocarbons. It also appears that the concentration of the usable hydrocarbons in the gross pyrolysis gases was relatively constant at about 7.5 to 10 mole percent, which suggested that the carrier gas could be used as a diluent to increase the weight of hydrocarbons produced. This molar concentration of usable hydrocarbons in the pyrolysis gases closely agreed with the 10 mole percent formed at 750°C (1382°F) without any carrier gas reported by Sanner, et al.(7). The effect of carrier gas composition was less than was expected.

After run 6 was completed, some additional inputs from the overall system viewpoint caused a significant shift in the effort. The excessive use of carrier gas was causing the product gas to consist of about two-thirds carrier gas and one-third pyrolysis products. This extra gas would place a large energy burden on the compressor and have an adverse effect on the potential energy conversion to gasoline. It was also recognized that the use of methane for a carrier gas would increase the amount of methane absorbed by the olefin absorber, which would increase the methane content of the purified olefins fed to the polymerizer. The presence of methane in the polymerizer would lower the effective pressure of the reactor and decrease yields. The ideal carrier gas would be either easily condensable (steam) or absorbed (carbon dioxide). Waste heat would be available to make process steam, and relatively pure carbon dioxide would be available from the pyrolysis gas clean-up process.

In the preliminary energy balance for the process, it was recognized that there would be a considerable amount of waste heat that could be recovered from the flue gases of the pyrolysis furnace and from the hot pyrolysis gases themselves. A review of these calculations showed there was enough energy to make process steam for use as carrier gas. As much as 1 to 1.5 kilograms of steam per kilogram of dry feed could be attained.

Steam

The capability of making superheated steam at pressures up to 1200 kPa (175 psi) was added to the pyrolysis setup and was first used with run 7. Since steam was not available at the building, a steam generation system was constructed to use distilled water. This system consisted of a tank of water pressurized to about 1380 kPa (200 psi) with nitrogen. The pressurized water flowed through a metering valve and a flowmeter before leaving the control room. The water then was flashed to steam inside a 1.3-centimeter (1/2-inch) diameter 304 stainless steel tube coiled inside of the pyrolysis kiln, as shown in Figure 6. Instability in the steam pressure led to the addition of a stainless steel steam accumulator chamber about 5 centimeters in diameter and 25 centimeters long. The accumulator damped out the pressure surges considerably. This system delivered superheated steam at up to about 1,000 kPa (150 psig) and 750°C (∿1400°F).

The method of injecting the steam into the feed and carrier stream was found to be fairly critical in that if the steam backed up into the solids feed system, the feed system became badly plugged with wet feed. To avoid the steam backing into the feeder, the steam ejector was located just barely upstream of the point where the carrier gas and feed stream entered the ejector housing, as shown schematically in Figure 8. As long as the steam temperature was in excess of 650°C (∿1200°F), very little problem was encountered with partially pyrolyzed feed adhering to the steam injector tube. The steam ejector was able to produce about 100 centimeters of water column pressure when the feeder pressure was atmospheric (±2 centimeters of water). This pressure differential generated by the steam ejector was sufficient to overcome the frictional pressure losses in the system prior to the accumulation of tars in the tubing during a pyrolysis run. An ejector orifice diameter of about 0.25 centimeter was finally used; it allowed steam flow rates of up to 6 kg/hr at about 450 kPa (∿65 psig). The downstream throat was 1.1 centimeters in diameter.

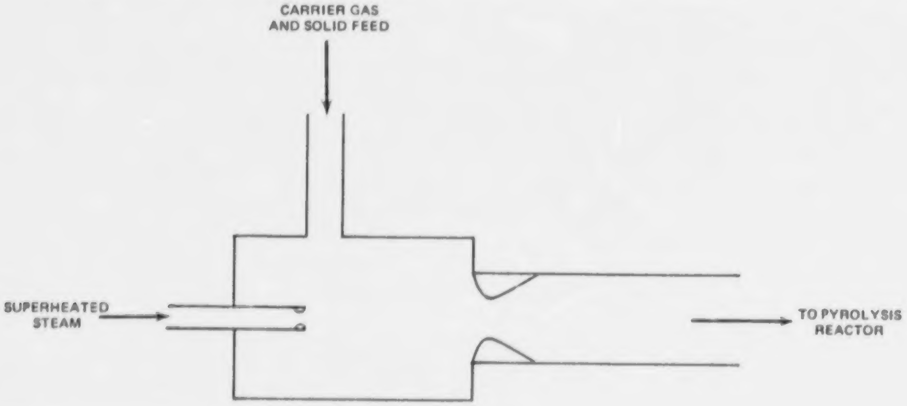


Figure 8. Steam Ejector Schematic

An attempt was made to pyrolyze with only steam as the carrier gas. This resulted in some of the steam condensing in the VibraScrew feeder. Wet feed does not flow through the system, so it plugged immediately. Run 7 was made using carbon dioxide as the fluidizing gas stream and steam as the ejecting stream. A short run resulted, with an encouraging gas analysis being made, but the data were insufficient for mass balances. The next several runs were made to evaluate potential methods of using steam as a carrier gas without it condensing on the incoming feed and causing the feeder to plug up. This method led to a compromise solution in which a minimum amount of carbon dioxide was used to fluidize the feed and to pump it through a venturi throat to the steam ejector, which boosted the flow into the pyrolysis reactor. Runs 14 through 19 were made with this arrangement as depicted in Figure 6.

After the steam ejection system was resolved, a series of runs was made to evaluate the combination of steam and carbon dioxide as carrier gases at retort temperatures from 552 to 860°C (1025 to 1580°F). A value of about 0.95 m^3 steam (15.6°C, 101 kPa (14.7 psi)) per kilogram of dry feed was used for most of the runs. This is equivalent to about 0.62 kilogram of steam per kilogram of dry feed. The CO_2 flow rate was maintained at about 0.15 m^3/kg dry feed. In comparison, there was between 0.11 and 0.46 m^3 net pyrolysis gases produced per kilogram of dry feed during the runs. The weight conversions of ECO II to ethylene, propylene, etc., was not greatly different from those of previous runs made with other carrier gases (hydrogen, carbon monoxide, and/or methane).

With the long-residence-time reactor (including the large cyclone), there were very definite trends of products with pyrolysis temperatures, with the most pronounced difference being between the lowest-temperature run at 552°C and the higher-temperature runs. The lowest-temperature pyrolysis was significant in that the gasification was very small; large amounts of char were recovered, and seemingly large amounts of water-soluble products and sticky tars were recovered in the water jug. These tars had a very pungent and obnoxious odor. In contrast, the higher-temperature pyrolysis runs produced qualitatively less water-soluble products that had only a mildly unpleasant odor. A summary of pyrolysis data was listed in Table 3.

The production of the desired olefins was affected by the pyrolysis temperature as shown in Figure 9. The production of ethylene generally increased with temperature, whereas that of propylene and butylenes decreased. Although it is possible that some of the propylene and butylenes were themselves pyrolyzed at the higher temperatures to account for the increase in ethylene production, data in the literature(19) suggest that these olefins as well as ethylene were more likely polymerizing at these conditions to form a mixture containing about half benzene and half "coal" tars. The increase with temperature of the unknown material, backflushed by the gas chromatograph and labeled "$C_5^=$+ C_6+", suggests that this polymerization may indeed have taken place. The location of the cyclone separator in the pyrolysis furnace gives the gases a calculated residence time of 4 to 5 seconds, which appears to be long enough for the pyrolysis gases to be significantly polymerized. Although the program goal was to polymerize the gaseous pyrolysis products, the production of large amounts of by-product "coal" tars by thermal polymerization at low pressures was deemed unacceptable. The lowering of the cyclone separator temperature to some temperature low enough to preclude polymerization during pyrolysis and yet high enough to prevent tar condensation was indicated.

An examination of the by-product fuel gas production (methane, carbon monoxide, and hydrogen) from runs 17 and 19 showed them to be "medium Btu" gases having a higher heating value of about 16.8 MJ/m^3 (450 Btu/ft^3). The lower heating value was about 15.9 MJ/m^3 (425 Btu/ft^3). The by-product gases from the milder 682°C pyrolysis (run 17) contained a lower total heating value of 4.4 kJ/g dry feed (1872 Btu/lb) while that from the more intense pyrolysis at 860°C (run 19) contained 6.9 kJ/g dry feed (2979 Btu/lb). These gases could be used in stationary internal combustion engines or turbines to provide shaft power for the process. The heating value of the by-product gases is only slightly below that of "town's" gas (higher heating value of 17.6 MJ/m^3 (475 Btu/ft^3)), reported to have been used with good success for a 15-kW (20-hp) engine after an increase in the compression ratio.(20) In any case, the by-product gases should perform much better than the pyrolysis gases used in Europe during the 1930s which had a calculated heating value of 3.9 MJ/m^3 (106 Btu/ft^3). These gases were made in stoves mounted on the vehicle by the partial oxidation of wood with air. The combustible constituents were reported to be 30% carbon monoxide and 1% methane. Compressed "town's" gas having a heating value of 11.1 to 14.9 x 10^6 J/m^3 (300 to 400 Btu/ft^3) was also used satisfactorily for motor vehicles at that time.(21)

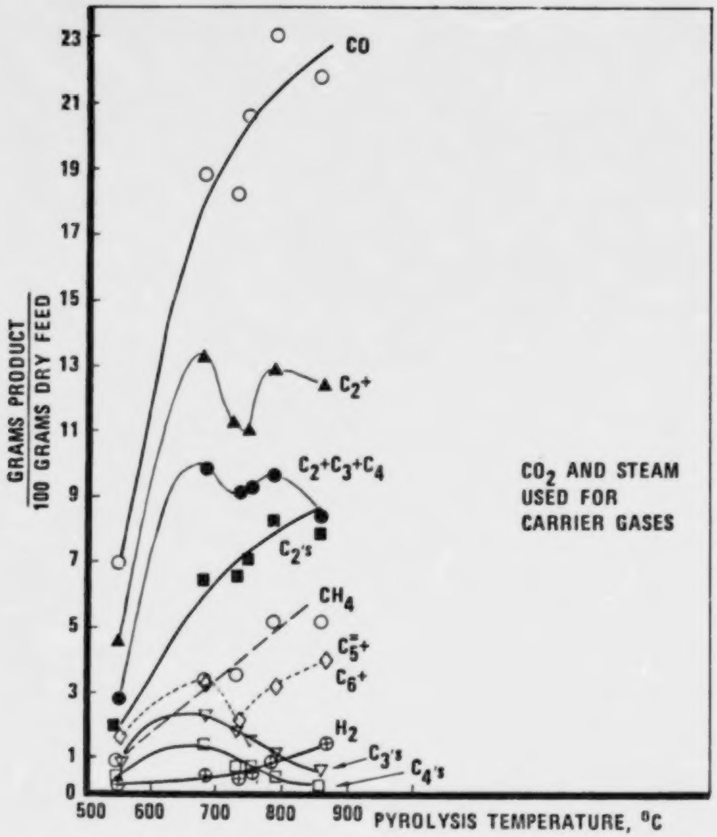


Figure 9. Pyrolysis Products vs. Pyrolysis Temperature with the Long-Residence-Time Reactor.

Samples of char from run 17 (682°C) and run 19 (860°C) were run for heat of combustion in a Parr bomb. A value of 17.9 kJ/g (7710 Btu/lb) was reported for the char from the lower temperature pyrolysis, and a value of 15.1 kJ/g (6504 Btu/lb) was reported for the char formed at the higher temperature. This trend is consistent with the greater gasification occurring at the higher temperature. Based on the weight of the ash recovered from these tests, the char from run 17 contained 58.7% ash and that from run 19 contained 50.1%. Based on the ash content of the feed, run 17 should have produced 16.6% char compared to the measured 18.9%. The tendency of the ash to melt to a slag indicates that the pyrolysis furnace operating at slagging conditions (about 1200°C or 2200°F) could melt the voluminous ash and form a high-density slag for ease of disposal.

As indicated previously, the use of steam and carbon dioxide as carrier gases, rather than hydrogen, methane, and/or carbon monoxide, did not appear to result in major shifts of the weights of desired pyrolysis products. To verify this observation, run 20 was made using a carrier gas consisting of steam and a mixture of 19% by volume hydrogen, 39% carbon monoxide, and 42% methane. The pyrolysis products from this run were not greatly different from those made using steam and carbon dioxide except that the C_2+ hydrocarbons were all slightly lower than usual. It appeared that if there is a small effect of carrier gas on the desired products, carbon dioxide is a preferred carrier gas. This implied that an important function of the carrier gas is one of diluting the products to decrease polymerization and subsequent tar formation during pyrolysis.

The use of steam as part of the carrier gas allowed the system to operate with a decreased noncondensable carrier flow rate and decreased the eventual dilution of the C_2+ hydrocarbons with carrier gas. This was primarily responsible for an average 40% increase in the C_2+ volumetric composition of the pyrolysis gases. Since the carbon dioxide carrier gas will be removed in the high-pressure scrubber, the C_2+ volumetric content of the gases (made with carbon dioxide carrier gas) fed to the olefin absorber will be over 200% greater than it would be with the use of only noncondensable carrier gases. This greater C_2+ concentration will allow the olefin absorber to have a higher efficiency in olefin recovery and result in less methane and/or hydrogen finding its way into the polymerizing reactor.

Short-Residence-Time Tubular Reactor

It was realized that the product gases were being held at the pyrolysis temperature for such a long time (∿5 seconds) that a portion of the olefins was polymerizing to tars and char. A 1.9-centimeter (3/4-inch) diameter stainless steel tube, 6.1 meters (20 feet) long was formed into a 41-centimeter (16-inch) diameter coil for the new pyrolysis reactor as shown in Figure 10. This resulted in a calculated residence time in the pyrolysis coil of about 150 milliseconds with the flow rates then in use. A thermocouple probe was placed at the exit of the pyrolysis coil so that the pyrolysis products impinged upon it. The product gases were then to be passed through a 1.2-meter (4 foot) length of noninsulated 1.9-centimeter (3/4-inch) tubing which cooled the gases below 537°C (1000°F) before they entered the 38-centimeter (15-inch) diameter cyclone separator. The cyclone separator was moved out of the kiln. The steam accumulator was moved to inside the pyrolysis kiln and the steam lines were shortened and better insulated; these changes produced much higher steam temperatures (approaching the pyrolysis temperature). The cyclone and the length of tubing connected to the quench jug were insulated with fiberglass. Runs 21 through 25 were made with this arrangement. The pyrolysis results for the entrained tubular reactor are shown in Table 4.

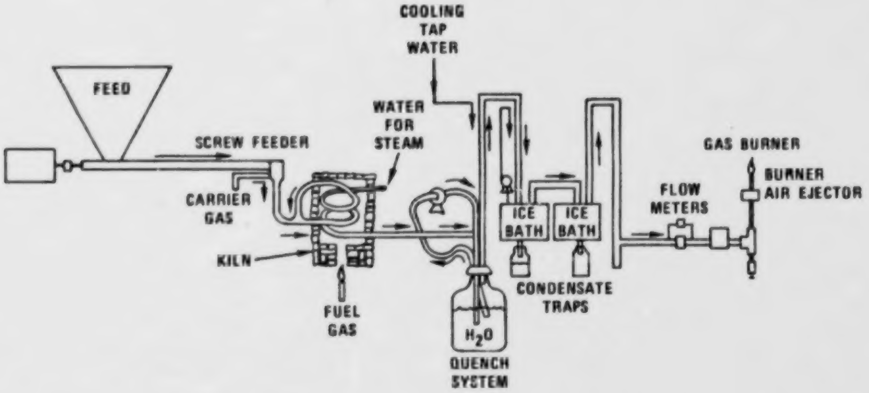


Figure 10. Entrained Tubular Pyrolysis Reactor.

TABLE 4. PYROLYSIS SUMMARY FOR THE TUBULAR REACTOR

Run	Length of pyrolysis reactor, m	Lot	Wt. % H_2O in feed	Pyrolysis temp, °C	Kg wet feed/hr	Carrier gas, m^3/kg dry feed	Steam,* kg/kg dry feed	Dry feed,** g/m^3 gases	Residence time, sec	Grams product/100 grams dry ECO II											Comments
										CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_5+ C_6+	H_2	CO	Char	
21	6.1	T-51	1	700	2.84	0.40	1.0	126	0.195	5.6	0.5	7.6	0.7	2.8	0.6	2.2	3.5	0.7	29.6	11.7	
22	6.1	T-51	1	740	4.22	0.25	0.7	172	0.178	3.2	0.5	6.1	0.5	2.1	0.1	1.7	3.2	0.5	22.0	#	
23	6.1	T-51	1	810	3.09	0.31	0.9	120	0.171	4.2	0.6	8.1	0.8	3.3	0.2	2.5	1.8	0.7	30.1	#	
24	6.1	T-51	1	750	3.13	0.54	1.2	95	0.133	5.1	0.8	9.4	1.0	3.3	0.2	2.2	3.2	0.8	36.8	23.0	
25	6.1	T-51	1	730	1.77	0.95	2.4	56	0.139	4.5	1.0	11.4	0.9	3.9	0.2	2.5	3.4	0.9	35.9	#	
26	2.1	T-51	1	~600	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	Smelly tars
27	2.1	T-51	1	730	3.43	0.49	1.1	111	0.050	2.5	0.5	6.7	0.6	2.0	0.1	1.8	3.7	0.6	22.2	16.1	
28	2.1	T-51	1	780	1.86	0.90	1.9	62	0.052	3.5	1.3	9.4	0.6	2.3	0.1	1.5	3.0	0.9	27.4	12.5	
29	2.1	T-51	1	770	2.31	0.88	1.6	68	0.045	5.2	1.6	9.5	0.9	2.5	0.1	2.5	1.9	1.2	42.5	22.7	N_2 carrier†
30	2.1	T-51	10	760	1.91	0.98	2.3	56	0.049	4.1	1.2	11.3	0.7	2.3	0.2	2.1	5.0	0.9	34.8	17.9	
31	2.1	T-51	10	720	2.16	0.87	1.9	67	0.053	3.1	0.9	9.1	0.8	2.0	0.1	2.0	5.8	0.7	27.1	12.7	
32	2.1	T-51	10	700	2.14	0.88	1.9	68	0.054	3.0	1.0	9.1	0.7	2.4	0.1	2.4	3.9	0.7	27.0	14.3	
33	2.1	T-51	10	760	2.34	0.80	1.8	68	0.049	3.8	1.2	10.5	0.8	2.5	0.1	2.3	2.3	0.8	32.3	20.4	
34	2.1	T-51	10	830	2.72	0.69	1.6	70	0.044	4.3	1.4	10.7	0.7	2.0	0.1	1.8	2.9	0.9	34.7	10.3	No cyclone
35	2.1	T-51	10	810	2.12	0.89	2.3	55	0.043	3.9	1.4	10.7	0.8	1.7	0.1	1.5	5.2	1.0	32.3	17.2	
36	2.1	T-51	10	820	2.57	0.71	1.7	66	0.044	4.6	1.3	10.3	0.8	2.4	0.1	2.0	2.9	1.0	38.3	#	(Char includes tars)
37	2.1	T-51	10	820	3.47	0.54	1.2	86	0.042	3.9	1.3	9.1	0.7	1.6	0.1	1.6	3.4	0.9	30.2	25.0	
38	2.1	T-51	10	770	3.79	0.49	1.1	102	0.046	3.3	0.5	8.1	0.4	2.8	0.2	2.4	4.4	0.7	29.6	17.2	
39	2.1	T-51	10	840	2.20	0.84	1.9	60	0.046	4.5	1.4	10.0	0.6	2.1	0.1	1.4	2.8	1.1	34.3	18.2	
40	2.1	T-51	10	750	2.29	0.82	1.8	69	0.051	3.3	1.1	9.2	0.8	2.8	0.1	2.4	3.9	0.8	29.6	15.8	
41	2.1	T-47	10	743	2.36	0.63	1.7	78	0.056	1.6	0.7	6.0	0.5	1.0	0.1	1.0	2.1	0.3	13.2	#	
42	2.1	T-47	10	732	2.75	0.62	1.5	96	0.059	2.7	0.9	7.5	0.7	2.0	0.1	2.0	3.4	0.5	22.8	#	
43	2.1	T-47	10	760	1.25	0.67	3.1§	48	0.064	3.1	1.2	8.7	0.5	1.6	0.1	1.9	2.8	0.6	22.9	20.2	
44	2.1	T-47	10	738	3.42	0.42	1.2	112	0.055	3.5	1.1	8.8	0.6	2.2	0.1	2.2	4.4	0.6	26.4	#	
45	6.1	T-47	10	871	4.34	0.20	0.9§	...	...	...	...	...	...	...	...	...	...	...	...	...	
46	6.1	T-47	10	761	0.84	1.00	4.7§	33	0.198	6.2	2.1	13.5	0.6	1.7	0.1	1.8	3.1	1.0	36.4	#	
47	6.1	T-47	10	759	3.81	0.39	1.0§	121	0.161	4.1	0.9	8.8	0.7	2.3	0.1	2.1	3.4	0.6	26.0	18.5	

*Includes steam from moisture in feed.

**Includes steam, carrier, and pyrolysis gases, all at pyrolysis temperature.

#Data not available.

†All runs except run 29 used CO_2 as the carrier gas. (9.6 g CO_2/100 g dry ECO II produced in run 29.)

§Variable steam pressure and flow.

As will be discussed in detail, the data suggested that the residence time in the pyrolysis coil was still too long, so a 2.1-meter (7-foot) length of tubing was shaped into a shorter reactor. This length of coil resulted in a calculated residence time of about 50 milliseconds. The kiln was rebuilt at that time to provide higher pyrolysis temperatures. Run 26 was only a check-out run with this new coil. Runs 27 through 44 were conducted with this shorter reactor tube. The large cyclone was removed after run 33 so that, through run 47, the char and tars were both collected in the quench jug, as shown in Figure 10.

Twenty pyrolysis runs were made using drum T-51 ECO II (a product of Combustion Equipment Associates) for the feed stock with the long tubular pyrolysis reactors, as shown in Table 4. These experiments resulted in the realization that between 700 and 840°C (∿1300 to 1550°F) pyrolysis temperature has a relatively minor role in affecting the pyrolysis products with residence times less than 150 milliseconds. The controlling variable appears to be definitely related to the relative concentration of the feed or more specifically the partial pressure of the pyrolysis gases in the reactor. Figure 11 shows that with the 6.1-meter (20-foot) pyrolysis coil there is a pronounced relationship of weight of product as a function of the weight of feed per cubic meter of pyrolysis gases (at the pyrolysis temperature). Figure 12 is similar but shows data generated with the 2.1-meter (7-foot) pyrolysis coil. In both cases, the more dilute pyrolysis conditions gave rise to a greater proportionate production of desirable hydrocarbons as well as to carbon monoxide and hydrogen by-product gases. Initially it was assumed that the increased hydrocarbon yields were due to a decreased residence time in the reactor. However, when the 2.1-meter coil replaced the 6.1-meter coil and reduced the residence time by two-thirds with no further increase in hydrocarbon production, it was realized that dilution was the key variable. In fact, the longer coil produced slightly greater amounts of products at the same dilution values, indicating more complete pyrolysis of the larger feed particles. The residence times indicated were calculated using a very simplistic approach; the volumetric flow rates of the gross pyrolysis gases and the steam (at the pyrolysis temperature) were divided into the volume of the pyrolysis reactor. The pyrolysis temperature was simplistically chosen to be that of the gas stream exiting the reactor.

The minor role played by temperature in this "high temperature" pyrolysis regime is seen in Figure 13. With a variation in pyrolysis temperature of nearly 150°C (270°F), there appears to be an increase in the ethylene production of perhaps 10%, but no significant increase in overall (C_2+ C_3+ C_4) nor C_2+ fractions was observed.

The use of nitrogen as the carrier gas in run 29 was made primarily to determine if the increase in the amount of carbon dioxide carrier gas was responsible for the apparently large increase in ethylene formation. The gas chromatograph, used for the analysis, elutes ethylene immediately after carbon dioxide, and there is some overlapping of the two peaks. There was concern that part of what was thought to be the ethylene peak was actually only carbon dioxide. The use of nitrogen as the carrier gas resulted in a relatively small amount of carbon dioxide in the gross gases (3% by volume) and good peak separation, but did not adversely affect the apparent production of ethylene. It was concluded that the ethylene data were valid. This same run did alter the interpretation of the propane and propylene data and resulted in their values

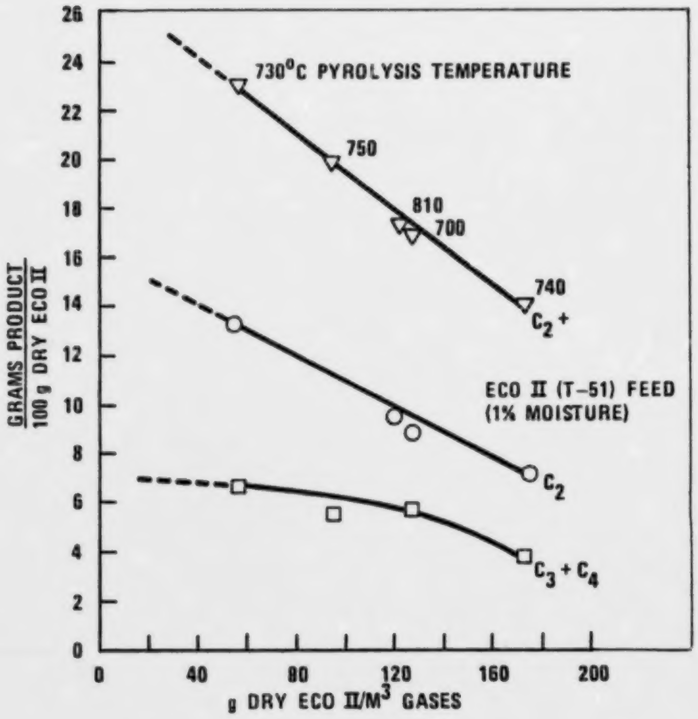


Figure 11. Products vs. Concentration in 6.1-meter Reactor.

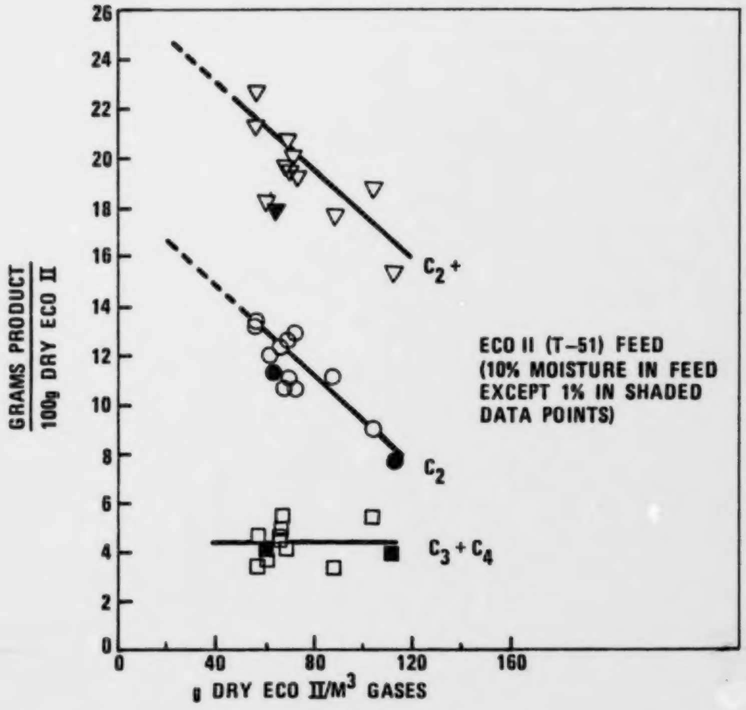


Figure 12. Products vs. Concentration in 2.1-meter Reactor.

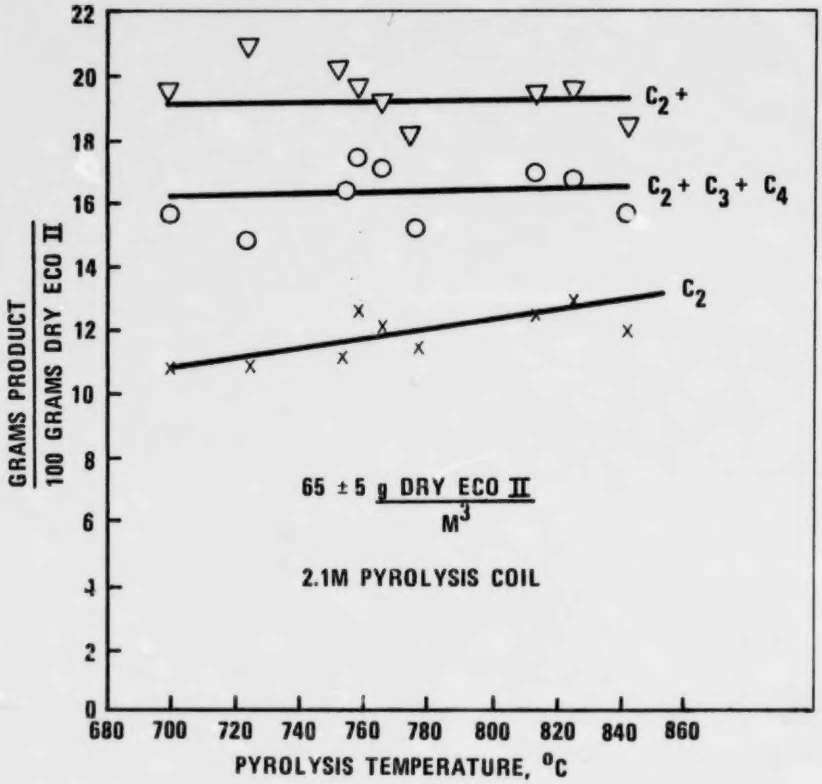


Figure 13. Products vs. Temperature.

being reduced slightly. These results are reflected in the data presented after run 20. No major shifts in the C_2+ hydrocarbon fraction were observed in changing the carrier gas from carbon dioxide to nitrogen in the run. There did appear to be significant increases in the carbon monoxide and hydrogen production with this run and a reduction in the amount of C_5+ material.

The variable partial loss of the carbon dioxide carrier gas backing up through the feed hopper makes the carbon and oxygen balances relatively unreliable. The use of steam in the pyrolysis process and water in the quench system makes the hydrogen balance difficult also. An examination of run 29, which used nitrogen as the carrier gas, shows good closure on the overall mass balance (1.006 kilograms out per kilogram in) and the carbon balance (1.018 kilograms out per kilogram in). The amount of water formed by pyrolysis needed to close the hydrogen balance is 0.108 kilogram of water per kilogram of dry feed. The oxygen balance very nearly closes without the hypothesis of water formation; i.e., 0.975 kilogram oxygen out per kilogram oxygen in or 0.009 kilogram water per kilogram of dry feed. Small differences in feed composition and/or a small error in the relatively difficult hydrogen analysis of the feed probably account for these discrepancies.

Experimental pyrolysis runs were conducted to evaluate the use of a different lot of ECO II feed (lot T-47), the reduction of the amount of carbon dioxide carrier gas used, and the use of the longer 6.1-meter pyrolysis coil.

Lot T-47 of ECO II appeared to be similar to the T-51 lot; but with some differences: 188 μm (T-47) vs. 270 μm (T-51) average particle size; 12.5% ash vs. 9.7% ash; and a heat of combustion (higher heating value) of 19.8 kJ/g (8507 Btu/lb) vs. 22.2 kJ/g (9550 Btu/lb). There had been some concern that the lower heating value for lot T-47 was indicative of a lower plastics content and that this would result in a significantly lower yield in desirable hydrocarbons, since plastics like polyethylene are pyrolyzed at these conditions to form very high yields of desirable olefins such as ethylene and propylene. Taking the pyrolysis runs as a whole, it appears that the hydrocarbon production from lot T-47 is about equivalent to that from lot T-51, with the result that slightly better energy conversions were observed with lot T-47 due to the lower energy content of the feed.

The use of the longer pyrolysis coil for runs 46 and 47 confirmed previous runs (21 through 25) with respect to relatively good hydrocarbon production with a lower kiln temperature (ΔT) due to the larger heat transfer surface and residence time. In fact, it has been observed that the temperature of the exiting pyrolysis gases (measured with a sheathed thermocouple probe) tends to be 25 to 50°C hotter than the pyrolysis kiln (also measured with a sheathed thermocouple). This probably reflects a slightly exothermic pyrolysis reaction occurring at the elevated temperatures and/or large temperature variations within the kiln itself. Using lot T-47 feed with 10% moisture gave similar results on a dry feed basis as were obtained with lot T-51 having only 1% moisture, as shown in Figure 11.

In runs 43 through 46 the steam flow was irregular. The problem with the steam flow was in part due to the "weeping" of the steam pressure relief valve and in part due to a cracked fitting. This leakage and pressure fluctuation resulted in uncertainties in the actual dilution present in the pyrolysis reactor for these four runs. Run 47 had no known boiler water leakage, although the steam pressure still had considerable fluctuation (125 ± 25 psi). The steam fluctuation was apparently due to a small change in the boiler waterline which allowed the water to accumulate in a horizontal section until the surface tension was overcome and the water was dumped into the hot section of the boiler. These factors resulted in variable steam flows, which were averaged for the purpose of comparing the runs.

The compositions of the pyrolysis gases after run 47 were qualitatively the same as previously noted, except that the carbon dioxide content was lower due to the decreased size of the feed transfer tube diameter. However, since the major objective of the pyrolysis runs was to provide gas to the compressor for purification system debugging, the quantitative aspects of the runs were secondary. Since the pyrolysis data were therefore of questionable quantitative validity, they are not presented.

After more analysis of the pyrolysis data, the longer 6.1-meter coil was felt to be the better length since longer residence times were available to more completely pyrolyze the larger feed particles and/or greater mass throughput capability was attained. The longer coil also had the advantage that the temperature of the kiln did not need to be so much greater than the pyrolysis temperature due to the increased heat transfer surface.

Low-Pressure Pyrolysis Gas Cleanup and Compression

As the pyrolysis gas stream exits from the pyrolysis reactor at about 750°C (~1400°F), it contains fine char, tar vapors, steam, carrier gas, and the pyrolysis product gases. The first three mentioned components are separated from the pyrolysis product gases at low (atmospheric) pressures.

The removal of the char for the first 33 runs was done with a 38-centimeter (15-inch) diameter by 38-centimeter high stainless steel cyclone separator that had been made for another project. During the first 20 pyrolysis runs, this cyclone was placed in the pyrolysis furnace and was serving both to pyrolyze the feed and to separate the char from the gases (see Figure 6). The cyclone was then moved out of the pyrolysis unit and insulated with fiberglass. Between the pyrolysis furnace and the cyclone was a short length of 1.9-centimeter (3/4-inch) stainless steel tubing in which the pyrolysis stream cooled to about 550°C (~1000°F). This large diameter, insulated cyclone was used for pyrolysis runs 21 through 33.

The existence of this large cyclone in the pyrolysis unit was questioned. Although it separated most of the char from the product gas, it did result in a relatively slow cool down of the gases. Also, inability to preheat the cyclone resulted in large amounts of steam condensing in the cyclone, and the char became quite wet. Also, significant deposition of char and tar in the long tube connecting the cyclone to the quench jug caused a large pressure drop in the system to develop during a run. Consequently, the cyclone was removed and runs 34 through 47 were performed with the system shown in Figure 10. This arrangement resulted in the char being collected in the quench jug. The char was filtered and air dried before weighing.

In order to have the experimental pyrolysis system be more realistic with respect to char separation, a smaller 7.6-centimeter (3-inch) diameter straight-sided cyclone separator having a 51-centimeter (20-inch) length was added to the system between the pyrolysis reactor and the quench jug after run 47. An electric heater was used to preheat the cyclone to prevent the condensation of tar vapors and steam during the start-up of the system. The char-laden pyrolysis gas stream entered the cyclone at about 400°C (750°F) with the steam, pyrolysis gases, and tar vapors leaving the top of the separator at about 320°C (~600°F). The cyclone design was reported* to achieve a 98.4% recovery of the 7.5 μm particles having a specific gravity of 2.5. This cyclone would then be expected to recover nearly 100% of any particles larger than 10 μm, whereas the recovery sharply drops for the smaller particle sizes; e.g., 75% of 25 μm particles. The char particles dropped down from the cyclone to an insulated conical container having a volume of about 28 liters (1 cubic foot). The temperature of the collected char was about 200°C, which was hot enough to prevent steam and tar condensation on the char. Only the very fine "talcum powder" sized char appeared to be carried over to the quench system. This experimental pyrolysis system is shown in Figure 14.

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*Private communication with Dustex Corporation.

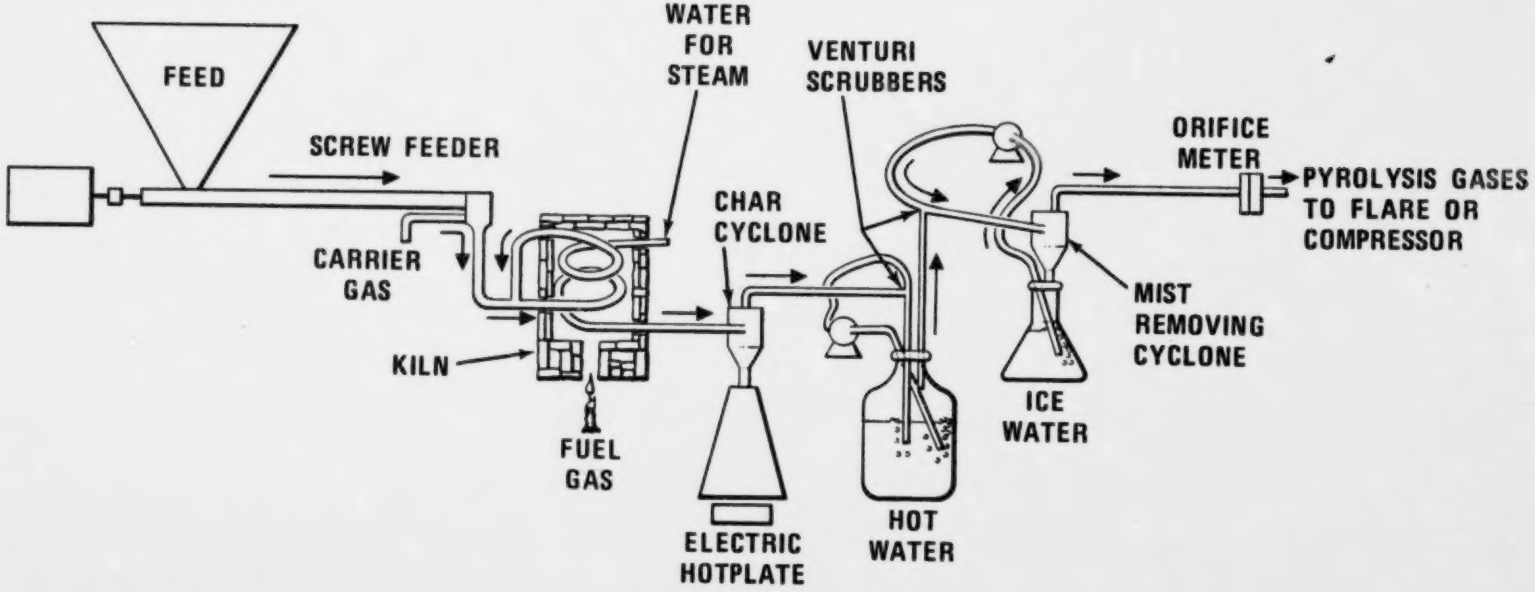

FEED
SCREW FEEDER
CARRIER GAS
KILN
FUEL GAS
WATER FOR STEAM
CHAR CYCLONE
ELECTRIC HOTPLATE
VENTURI SCRUBBERS
HOT WATER
ICE WATER
MIST REMOVING CYCLONE
ORIFICE METER
PYROLYSIS GASES TO FLARE OR COMPRESSOR

Figure 14. Pyrolysis Schematic with Small Cyclone.

After the cooled char had been transferred from the cyclone receiver to a weighing container, it remained in a loosely packed state for several minutes. After the collected char was allowed to stand for a few minutes, its apparent density was about 0.35 g/cc (22 lb/ft^3). After standing for about a week, the char had settled to a bulk density of 0.50 g/cc (31 lb/ft^3). This is nearly identical to the 0.48 g/cc for the relatively dense ECO II feed. The average amount of char recovered in runs 49 through 57 was 0.18 gram per gram of dry feed and varied from 0.16 to 0.19 gram per gram with a standard deviation of 0.01 gram per gram (six samples). This amounts to a feed-to-char volume ratio of 4 to 1 with little storage time or 5 1/2 to 1 with longer storage times. Combustion of the char would be expected to result in significant further reduction of the volume, particularly if the char were burned under slagging conditions. The apparent lack of change in the bulk density of the char relative to the feedstock would imply that the pyrolyzing particle does not retain its physical dimensions during pyrolysis in the entrained flow tubular reactor.

The tar vapors contained in the pyrolysis gases were a very real continuing problem. Since they are present in very small concentrations, the tar vapors do not condense to form a hot fluid but rather must wait until they are so cool that they condense to a high-viscosity, grease-like material. These condensed tars were deposited wherever the pyrolysis gases were cooled to the tar vapor's dew point. In the early runs, the tars condensed inside the 1.9-centimeter (3/4-inch) stainless steel tubing used to convey the pyrolysis products. This led to short pyrolysis runs as the tubing became rapidly plugged with tars.

Once the pyrolysis conditions were more favorable for gasification, rather than for tar production, it was hoped that the plugging problems would also be resolved. Although much better gasification conditions were achieved, the tars eventually accumulated and plugged the piping. The plugging was especially severe at 90-degree corners. The tubing with the 90-degree corners was replaced with an arched tube having a 60.96-centimeter (2-foot) radius which connected the gas outlet of the cyclone to the solvent trap. The tar-laden gases bubbled through an acetone solvent trap and were rapidly cooled, so that most of the tars remained in the solvent. This method also evaporated a considerable amount of solvent, most of which was recovered in the condensers. The condensed solvent formed a solution with the thick, viscous tars which was fluid enough to drain back to the solvent trap.

The tars were found to be soluble in both acetone and toluene at ambient temperature. Toluene was evaluated in the system prior to the use of steam, and although it potentially had the advantage of forming two phases (aqueous and organic), not enough water was formed during pyrolysis to create the aqueous phase. The toluene-tar solutions were accumulated in the condensers, which led to eventual plugging. Acetone was the best solvent found for the tar removal. Although water is soluble in the tar-acetone solution, the acetone acted as an "antifreeze" agent for both the tar and the water.

Installation of the solvent trap solved the problem of plugging downstream of the trap, but it also imposed an additional heat load to the condensers. This was resolved by cooling about 5 feet of tubing leading up from the solvent trap with tap water and the next 4 feet of tubing with brine at -7°C (20°F).

The cold brine was recirculated with a brass water-cooler pump, whereas the small amount of tap water required was allowed to run down the drain.

Upstream of the solvent trap, the tars still accumulated rapidly during start-up until the tubing was heated above the tar condensation temperature. A 6-foot-long propane tube-burner was fashioned into the shape of the arched tubing to preheat the arch immediately prior to the start of a pyrolysis run. This was very successful in eliminating the tar deposition, except for the very end of the tube which was immersed in the solvent. A means of insulating this 200°C (400°F) tube from the solvent-tar solution was partially solved by wrapping the tube with Teflon tape. The propane tube burner was later removed and the arch was insulated. Steam was then used to preheat the tube.

The collection of the tars formed during pyrolysis was greatly improved starting with pyrolysis run 6. Previously, acetone or toluene was used in the solvent trap, where the hot gases were bubbled through the solvent. This method had resulted in fairly good retention of the tars, but the heat transfer load to the condensers was higher due to the vaporized solvent. Even though the condensed solvent and tars were gravity-returned to the solvent trap, there was a net liquid volume loss. Also there was severe condensation of tars inside the gas-delivery pipe immersed in the solvent. It was realized that the use of acetone or toluene would not be a viable solvent choice for scale up, so water was selected for use in the solvent trap. Two other changes were made at this time. First, a recirculating pump was added to spray water into the hot pyrolysis gas stream about 30 centimeters (1 foot) upstream of the new solvent trap (a 19-liter (5-gallon) jug). This water quench system was first used in pyrolysis run 6 with good success although it slowly condensed tars immediately upstream of the water injection point. Second, the use of dry ice in the second condenser was changed to regular ice. The elimination of the dry ice stopped the plugging of that condenser with small ice or "snow" particles. This did not compromise the overall system goal since the hydrocarbons not condensed by the dry ice would be easily condensed after compression at the higher pressures. The water quench system also served to absorb the undesirable water-soluble products that would otherwise be carried along; e.g., HCl, H_2S, acetone, acetic acid, etc. The effect of the water quench system was to condense the hot tar vapors into tiny droplets, which were swept down the piping to the 19-liter jug where they were retained. Passing the quench water through a heat exchanger maintained the temperature of the water between about 70 and 90°C (160 to 190°F). At these temperatures some distillation occurred and the condensate from the ice trap appeared to be enriched with water-soluble organic material. No organic liquid phase was observed, since the high-molecular-weight liquid hydrocarbons (benzene, etc.) appeared to be too dilute to condense at 0°C.

After the pyrolysis gases left the solvent trap, they traveled to two condensers via 1.9-centimeter (3/4-inch) stainless steel tubing. These condensers were packed with 1.3-centimeter (1/2-inch) pieces of stainless steel pipe with an outside diameter of 2.1 centimeters (3/4 inch). The first condenser was ice cooled and the other was cooled by dry ice in acetone (regular ice was later used). Initially these condensers worked well, although it was observed that a gradual buildup of tars occurred. Attempts to remove the tars with acetone were only partially successful, and eventually the packed condensers were abandoned.

Although the preheated arched tube had some advantages over previous configurations, it eventually needed to be cleaned out. The long curved tube made this cleaning relatively difficult. At the time that the large cyclone was removed, the arched tube was replaced with a shorter length of tube which kept the pyrolysis products hot enough so that the tar vapors did not condense. The water quench stream was injected straight down into the quench jug at a point where the pyrolysis products made a 90-degree turn down into the quench jug. This was a fairly good system, but would eventually plug just upstream of the quench water injection point. In an effort to prevent tar condensation from occurring, the quench water injection location was moved to a hotter location, upstream to the exit of the char cyclone separator. This was a better location, but still resulted in eventually plugging of the system just upstream of the water injection point even when it was well insulated.

A stainless steel drum having a volume of about 50 liters (13 gallons) was modified for use as the quench water storage container as shown in Figure 15. This allowed the hot pyrolysis gases to leave the 1.9 centimeter tubing and be dumped into the drum where they could then be sprayed with the quench water. This method was promising, but still resulted in eventual plugging at the entrance to the quench drum. The system was modified to prevent the water spray from directly impinging on the entrance tubing and resulted in a very long run which was terminated because the pyrolysis gas surge tank was full and not because the system had plugged. Subsequent examination of the system has led to the addition of another quench water pump to double the flow as well as a filter at the exit of the quench drum consisting of a pad of continuous stainless steel turnings ("metal sponge").

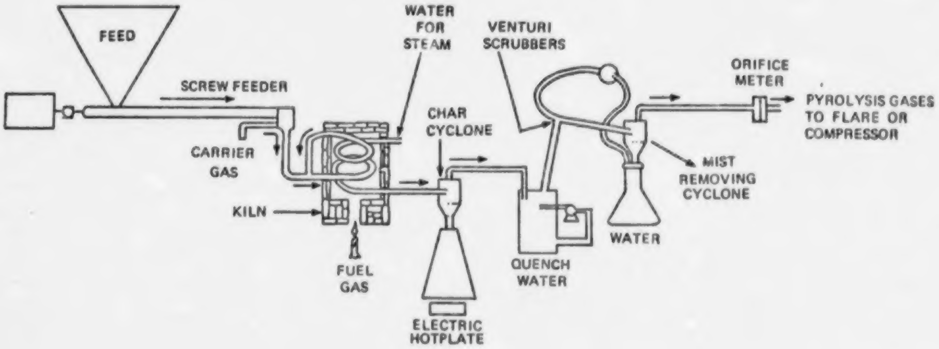


Figure 15. Final Pyrolysis Schematic.

When the smaller char cyclone was added to the system, another small cyclone was added to help demist the cooled pyrolysis gases downstream of the quench jug. This cyclone was about 7 1/2 centimeters (∿3 inches) in diameter and 25 centimeter (∿10 inches) long. Immediately upstream of the demisting cyclone, ice cold water was injected at a 90-degree elbow in the 1.9-centimeter tubing conveying the cooled pyrolysis gases. The effect of the additional water was to further cool the gases and to help coalesce the persistent mist particles. This system was relatively successful, but a filter was still necessary prior to the gases entering the compressor. The filter collected on the order of 1 cc of tar and water per kilogram of feed. An automotive spin-on oil filter was used to protect the compressor from the tar mist after run 67.

The use of ice to cool the demister water was stopped with no apparent adverse effects to the product or to the compressor, but the filter collected more liquid. On the order of 10 cc of condensate was recovered per kilogram of feed from the high-pressure pyrolysis-gas surge tank if the demister was not ice cooled. This condensate has two phases and extraordinary solvency power. The Buna-N O-rings in the check valve leading to the surge tank became swollen so badly that the check valve was unable to close properly. The condensate was also found to cause Viton^{TM} O-rings to swell nearly as badly, so the high-pressure check valve O-rings were finally changed to Teflon^{TM}. The Teflon O-rings in contact with the condensate appeared to be functioning well. The condensates were thought to be mixtures of pentane, benzene, toluene, water, and water solubles such as acetone and ethyl acetate. It may be possible to use one or both phases of the compressor condensates as the final low-pressure wash mediums, since this material is a mixture of aromatic and oxygenated, water-soluble solvents and has excellent solvency power.

The compressor functioned with no apparent problems as long as the oil filter was functioning. The three-stage compressor used was estimated to be 15 times larger than necessary for the pyrolysis gas flow rates. To avoid evacuating the pyrolysis system with this large compressor, a portion of the compressed pyrolysis gases was recycled to the compressor inlet. This was accomplished through the use of a very sensitive forward pressure regulator (often called a "vacuum" regulator). Once the recycle pressure regulator was set, the inlet pressure of the compressor was maintained without further manual adjustment even with large variations in pyrolysis gas flow rates. The compressed pyrolysis gases were stored in a spherical stainless steel tank having an estimated 34-liter capacity and a working pressure of about 16,500 kPa (2400 psi), although it is limited by the pressure relief valve to only 10,340 kPa.

Gas Flow Measurement

The pyrolysis gas flow measurement was accomplished initially with both a positive displacement gas meter designed for household propane (LPG) use and an orifice meter. The propane meter provided a convenient total gas flow, while the orifice meter qualitatively indicated the instantaneous gas flow rate during the pyrolysis run.

Until about pyrolysis run 40, it had been assumed that the LPG meter was functioning accurately since its action appeared good. A calibration check using both rotameters and the orifice meter showed that the gas meter was in error. For every cubic meter of gas indicated by the gas meter, 1.3 m^3 had actually passed. This resulted in apparently lower product values than was actually the case. The gas meter was disassembled, cleaned, and reassembled with no apparent accuracy improvement. Apparently the rubber bellows had swollen so that more gas was required to operate them. Since the orifice meter data had been recorded it was possible to calculate the volumetric flow. The computer program was modified to allow the input of the orifice meter data rather than the LPG meter indicated gas volume. All of the data after run 20 reflect the corrected gas volumes as obtained from the orifice meter. The LPG meter was removed from the system after run 40.

DISCUSSION OF SYSTEM

The evolution to a long tubular reactor resulted in a trouble-free, non-clogging pyrolysis unit. Coke deposits did not accumulate in the pyrolysis tube, probably because of the scouring action of the turbulently transported char. The eventual use of steam also precluded coke buildup in the pyrolysis tube, since any remaining coke was oxidized by the relatively slow "water gas" reaction to form carbon monoxide. The "water gas" reaction was too slow at these temperatures to significantly affect the rapidly flowing pyrolysis products,(22) but it would have had time to react with any coke or char adhering to the reactor wall. The steam also served to maintain a black iron oxide coating which prevented the iron from catalyzing coke-forming reactions.(23)

The tubular reactor was sucessfully used in pyrolysis runs in which the only steam present was that derived from the moisture in the feed (1 to 10% by weight). This occurrence indicates that the scouring action of the char alone was probably sufficient to keep the tubular reactor clean. No evidence of molten glass deposition in the reactor was seen, although it is probable that there were some fine glass particles in the ECO II feed. However, since the pyrolysis reactor was operated intermittently, air may have entered the reactor while it was still hot to oxidize any coke that had accumulated.

The use of an entrained particle, long tubular reactor was successfully demonstrated for the pyrolysis of finely ground organic wastes derived from municipal trash. The advantages of this type of reactor design are: its design is simple; it is easy to operate, with no sophisticated control systems (as compared to fluidized beds); high-density trash particles (e.g., dirt) do not accumulate in the reactor; and scale-up would be accomplished by having a large number of pyrolysis tubes in parallel rather than by using a large monolithic reactor (this would make future plant capacity increases relatively inexpensive). In comparing the entrained flow reactor with the simple slow, vertical shaft pyrolysis reactor, one may note that both must have a coarse shredder or grinder, a solids feeding system, a pyrolysis temperature control system, an ash or char removal system, and pyrolysis gas cleanup. The entrained reactor must in addition add only a secondary shredder and a carrier gas system. The added complexity needed to operate the entrained solids pyrolysis reactor is relatively small compared with the sophisticated systems needed to operate fluidized bed reactors being fed waste material having widely varying shapes, sizes, and bulk densities.

The entire pyrolysis system was manually controlled remotely from the control room located safely behind a barricade. The system was monitored by twelve recorded thermocouple channels, steam and carrier gas pressure-gauges, boiler water flowmeter, and five very low pressure gauges measuring inches of water. This experimental system was controlled and readings were taken by one operator with a small amount of assistance from a second man to take gas samples and to control the pyrolysis kiln temperature by manually adjusting the fuel gas pressure regulator. A thermostat to control the temperature of the kiln and an integrating recorder for the orifice meter would have been worthwhile improvements to the system.

DISCUSSION OF PYROLYSIS RESULTS

Based on the experimental results which favored olefin formation, a product weight distribution as shown in Figure 16 was obtained from the municipal solid waste feedstock used (ECO II). As has been discussed, this method of pyrolysis results in products that are characterized by a relatively high weight fraction of gasoline precursors and carbon monoxide, relatively smaller amounts of char and carbon dioxide, and very little methane and hydrogen. As shown in Figure 17, slightly more than half of the energy contained in the organic waste is recovered in the gasoline precursors. About one-third of the energy is recovered in the "medium Btu" by-product gas stream of carbon monoxide, methane, and hydrogen. About one-seventh of the energy is recovered in the char, which has a heating value similar to that of lignite coal.

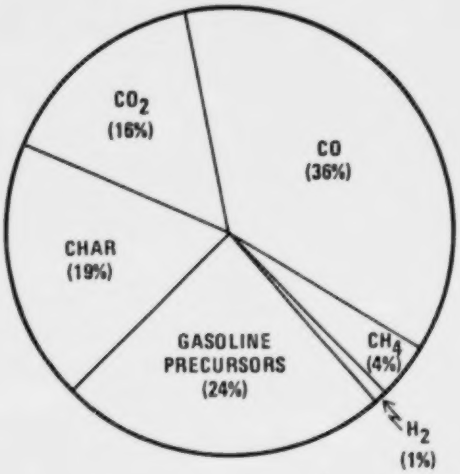


Figure 16. Pyrolysis Product Weight Distribution.

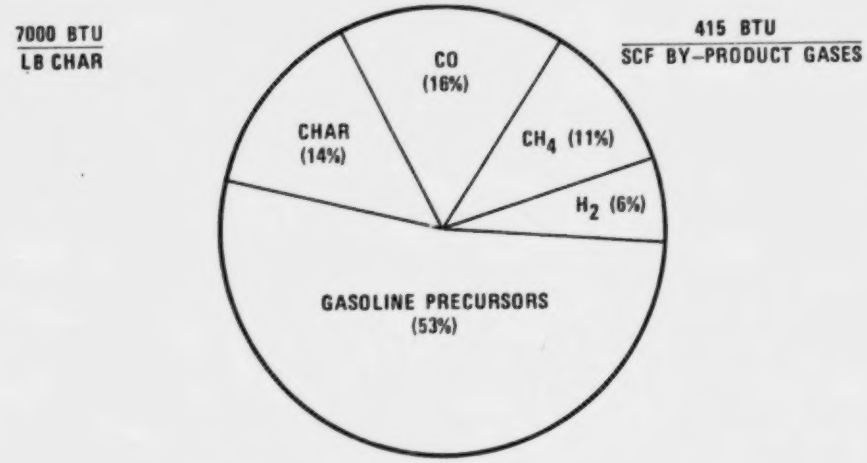


Figure 17. Pyrolysis Product Energy Distribution.

The by-product gas stream could be used to fuel stationary internal combustion engines or gas turbines, to generate shaft power for the compressors and shredders, as well as to fuel the pyrolysis furnace along with the by-product char. As was mentioned, the use of steam to dilute the pyrolysis gases results in a higher conversion to gasoline precursors by reducing secondary reactions. It now appears that the process will be optimized by making as much steam as possible by energy recovery from hot gas streams as well as by utilizing all of the char and the by-product fuel gases for process energy. This will result in only gasoline, "JP-5", and lubricating oils as the products from the organic fraction. These products will be readily marketable, in contrast to char, pyrolytic oils, or "medium Btu" gas.

The pyrolyzing or cracking of large hydrocarbon molecules (e.g., crude oil) to form smaller molecules (e.g., ethylene) has many strikingly similar features to the pyrolysis of oxygenated organic wastes as developed by this program. The use of steam to dilute the pyrolysis system and thus to enhance ethylene production has been used by the petroleum industry for over 20 years. Ratios of steam to feed were reported to be on the order of 0.9 to 1.8 kilograms of steam per kilogram of hydrocarbon feed,(24) which is similar to that used in the experiments discussed in this report. The contact time and temperature combinations to optimize ethylene production when pyrolyzing naphtha feedstocks range from about 1200 milliseconds at 800°C, to 30 milliseconds at 925°C. The latter combination carried out in long tubes, less than 5 centimeters in diameter, yields about 10 to 20% more ethylene and reflects the state-of-the-art.(25) The similarities of pyrolyzing naphtha and ECO II to form olefins are quite interesting and suggest that the ECO II is easier to pyrolyze than is naphtha and that the residence times calculated for the 2.1- and 6.1-meter pyrolysis reactors are credible. It follows that much of the technology developed by the petroleum industry for pyrolysis of hydrocarbons will be applicable to the pyrolysis of cellulosic feedstocks (MSW); i.e., long tubular pyrolysis reactors heated by combustion gases and/or steam which result in very short residence times.

Similarity of Pyrolysis Results

The experimental results indicate that a great similarity of products also exists with the steam-diluted, entrained-bed pyrolysis of oil shale(26) and of cellulosic wastes as determined by this trash-to-gasoline project. This similarity also holds true for the pyrolysis of naphtha to ethylene. To illustrate the similarities in the pyrolysis of naphtha, oil shale, and cellulosic organic wastes, the products of pyrolysis are shown for comparison in Figures 18, 19, and 9, respectively. In these figures are plotted the relative weights of various hydrocarbon products as a function of pyrolysis severity; e.g., temperature and/or residence time. It is interesting to note that the shapes of the product curves for ethylene, propylene, and butylenes are qualitatively quite similar for these greatly different feedstocks. This implies that the different feedstock molecules may be disintegrating into similar clouds of very reactive free radicals ($H\cdot$, $:CH_2$, $\cdot CH_3$, etc.) which then combine at very high rates to form similar product distributions. This free radical hypothesis of hydrocarbon pyrolysis has been discussed in the literature for many years.(27)

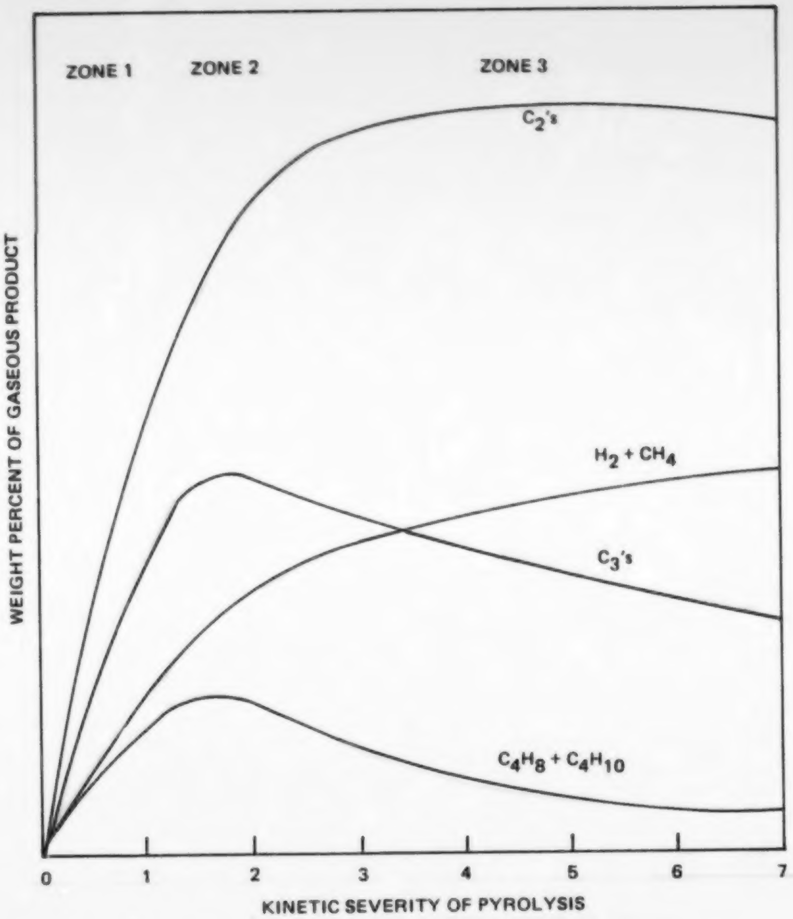


Figure 18. Naphtha Cracking Products. (28)

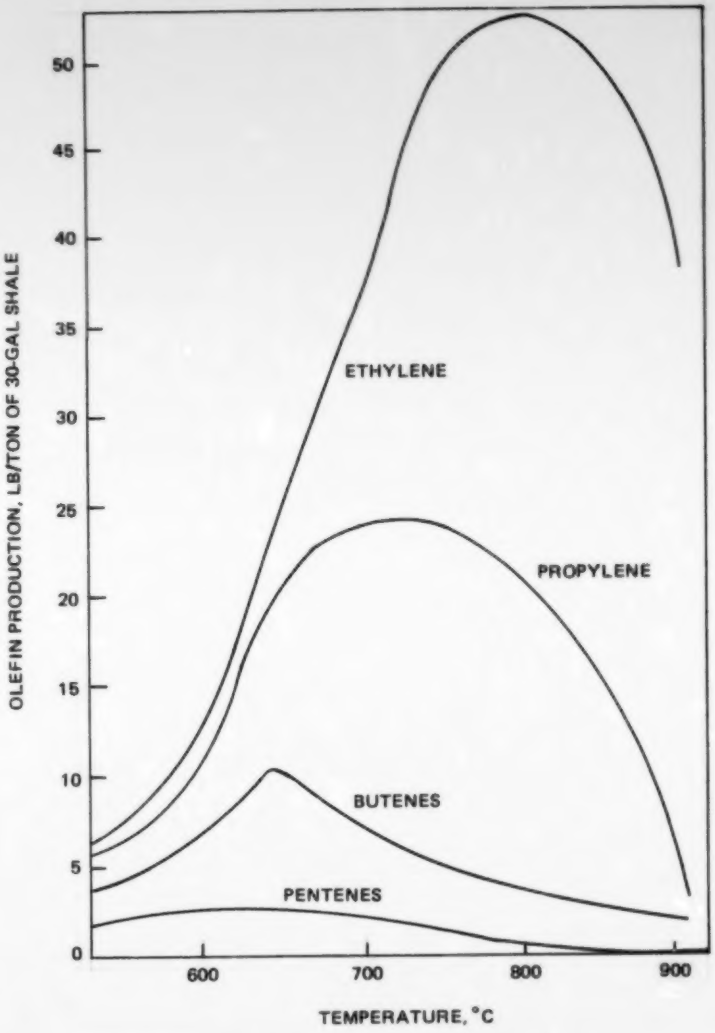


Figure 19. Oil Shale Pyrolysis Products. (26)

As was noted, the hydrocarbon product distribution formed by the pyrolysis of MSW (ECO II) is very similar in nature to that obtained from the "steam cracking" of naphtha or oil shale under similar reaction conditions.(28) The petroleum industry has long known that the presence of steam in the pyrolysis of hydrocarbons serves to dilute the system and thus to reduce secondary tar-forming reactions.(29) It is also known that the "water-gas" reaction to form hydrogen and carbon monoxide is too slow to be significant in the 700 to 850°C range of interest with short residence times of a few seconds or less.(22) (The water-gas reaction apparently is significant only in that it oxidizes carbon accumulating on the reactor tube walls.)(23)

Carbon dioxide in the steam cracking of naphtha is also known to be inert. For example, with the Union Carbide-Kureha crude oil cracking process, superheated steam is formed by the burning of a hydrocarbon fuel with oxygen to form a mixture of steam and carbon dioxide to which is added additional steam. The crude oil, or naphtha, is then injected into this hot gas stream and contacted for about 20 milliseconds before the reactions are quenched. The pyrolysis gases are later compressed to 2,070 kPa to remove the carbon dioxide with a modified alkanolamine solution.(30)(31)

In addition to the relative inertness of steam and carbon dioxide, the results of this program have shown that the use as carrier gas of nitrogen, methane, carbon monoxide, or mixtures of hydrogen, methane, and carbon monoxide had no significant impact on the hydrocarbon product distribution (except for methane, obviously). However, it was shown in this program that decreasing the concentration of the pyrolysis gases in the exit gas stream was an important variable drastically increasing the relative amount of ethylene produced in the product.

Relative Amounts of Gaseous Pyrolysis Products

As can be seen by examination of Table 5, carbon monoxide was the predominant gas specie by weight in the pyrolysis gases. For this reason, it was chosen as a basis of comparison to determine if the other gaseous products varied substantially relative to each other. Table 5 shows the molar quantities of the gaseous pyrolysis products relative to carbon monoxide. Interestingly enough, these ratios of products are considerably more constant than the overall yields per unit weight of feedstock. The most consistent ratios were those of carbon dioxide, methane, and ethylene, although the carbon dioxide consistency was based on only three experiments whereas the rest of the data was based on 53 experiments. (Since substantial amounts of carbon dioxide carrier gas were often lost in the feeding system, the vast majority of the experiments were unsuitable for the generation of quantitative carbon dioxide data.) The ratios to carbon monoxide of acetylene, ethane, propylene, the butenes, the $C_5^{=}+$ C_6+ fraction (presumed to be aromatics), and hydrogen were more variable due to their tendency to form secondary products or to be products thereof, depending upon the severity of the pyrolysis conditions.

The constancy of the pyrolysis gas composition suggests that those pyrolysis conditions which favored ethylene production were actually favoring the overall production of all gases. In Figure 20, it is seen that the same parameter that favored ethylene production did indeed also favor overall gasification. However, since the amount of char formed was fairly constant at

TABLE 5. GASEOUS PYROLYSIS PRODUCTS: MOLAR RATIOS AND WEIGHT-PERCENT

Product	Product, moles/moles CO	σ_x	$\frac{\sigma_x}{\bar{x}}$	N	Volume, percent	Weight, percent
CO	1.00	...	...	...	45.6	50.7
H_2	0.35	0.08	0.23	53	16.0	1.3
C_2H_4	0.28	0.05	0.18	53	12.8	14.2
CH_4	0.24	0.04	0.17	53	11.0	6.9
CO_2	0.16	0.02	0.13	3	7.3	12.7
C_3H_6	0.045	0.015	0.33	53	2.1	3.4
C_2H_2	0.035	0.010	0.29	53	1.6	1.6
C_4H_8	0.028	0.011	0.39	53	1.3	2.9
C_2H_6	0.019	0.005	0.26	53	0.9	1.0
C_5+	0.031	0.022	0.71	53	1.4	5.2

σ_x = standard deviation

$\frac{\sigma_x}{\bar{x}}$ = coefficient of variation

N = sample size

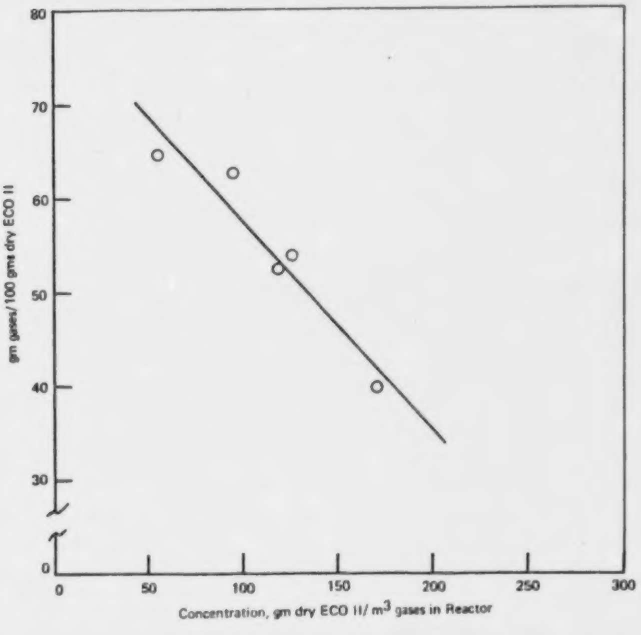


Figure 20. Gaseous Products (Except Carbon Dioxide and Water) vs. Concentration.

20 ± 5% by weight, the amount of tars, water and water-soluble organics must have varied accordingly to close the mass balance.

The average overall empirical formula for the gaseous pyrolysis products is very nearly the same as that for the ECO II feedstock. In fact, if the feedstock were to be completely gasified to the observed gaseous products, the elemental balances would be 95% closed for hydrogen and 106% closed for oxygen. This implies that the other pyrolysis products in the form of char, water, tars, and water-soluble, oxygenated organics would also have the same overall chemical composition as the feedstock.

If the dry, ash-free feedstock were to be completely pyrolyzed to the same average gaseous products, the ethylene yield would be 14% and the C_2+ yield would be 28% by weight. These approximate yields are predicted as maximum yield at infinite dilution, as can be seen in Figures 11 and 12.

Hypothesized Pyrolysis Mechanisms

Pyrolysis of cellulosic meterials appears to proceed via several different concurrent competing reactions whose relative rates are very temperature dependent. As indicated in Figure 1, at low temperatures the predominant reaction is one of dehydration to form char and water vapor. At intermediate temperatures, the predominant reaction is chain cleavage to form levoglucosan tars. However, above 650°C the gasification reactions to form combustible volatiles predominate.(32) These combustible volatiles include hydrocarbons, oxygenated organics, carbon oxides, and hydrogen. The change from the tar-forming reaction to the gasification reactions with sawdust is accompanied by a change in activation energy from 25 to 14 kcal/mole and the pre-exponential factor is reduced from 2.64×10^5 sec^{-1}. to 3.0×10^3 sec^{-1}. Apparently the reactions are still first order.(33) Of primary interest to this program were the hydrocarbons. The data generated in this program revealed that when the pyrolysis system was dilute, significantly more gases were produced. These gases had a relatively constant composition, although secondary reactions could shift the composition of some components. The overall elemental composition of the gases was remarkably similar to the feedstock, which indicates that the gasification reaction itself has at least two major competing reactions, as shown in Figure 21: (a) to form gases; or (b) to form relatively stable oxygenated compounds (many of which would be water soluble).

Gasification of an organic molecule involves the rupturing of the original bonds to result in smaller molecules and/or fragments of molecules called free radicals. As the original molecule is heated, low-level energy surges are thought to be traveling up and down the molecule. When the surges collide at a random location, sufficient energy would then be present at that random location to rupture the bond. If the material is heated slowly to an intermediate temperature, the energy surges could perhaps gain slowly in intensity until the weaker bonds were more selectively ruptured to form the levoglucosan tars widely reported. However, with rapid heating perhaps many more, larger energy surges are transferred to the molecule. The probability of random chain scission is thus increased, and the relative importance of levoglucosan as a pyrolysis intermediate is decreased. In any case, whether or not levoglucosan is a significant intermediate, it is thought that, at the thermal conditions employed in the process, the pyrolysis products rapidly form a primordial cloud of small molecular fragments or free radicals, many of which are oxygenated hydrocarbons as shown in Figure 22. If the reaction conditions are relatively low pressure and are dilute (low partial pressures), the free radicals are hypothesized to further pyrolyze with the formation of hydrogen and hydrocarbon free radicals as well as carbon oxides. The hydrogen and hydrocarbon free radicals would then randomly combine to form hydrogen, methane, ethylene, propylene, etc., as shown in Figure 23. At pyrolysis temperatures above 700°C, the primary pyrolysis products begin to immediately polymerize to form secondary products such as benzene, styrene, and toluene, as well as multiple ringed aromatic tars as shown in Figure 24. (Using a long residence time of a few seconds to crack hydrocarbons leads to the evolution of hydrogen and an aromatic product containing about 50% tars.)(34) If the pyrolysis products are held for an extended period of time, the aromatic products continue to grow in size to form macromolecules containing very little hydrogen, which are known as carbon black as shown in Figure 25. Part of the char could thus be derived from the aromatic pyrolysis products. The dilution of the pyrolysis reaction serves to minimize the secondary tar and char forming reactions involving the olefins.(29)

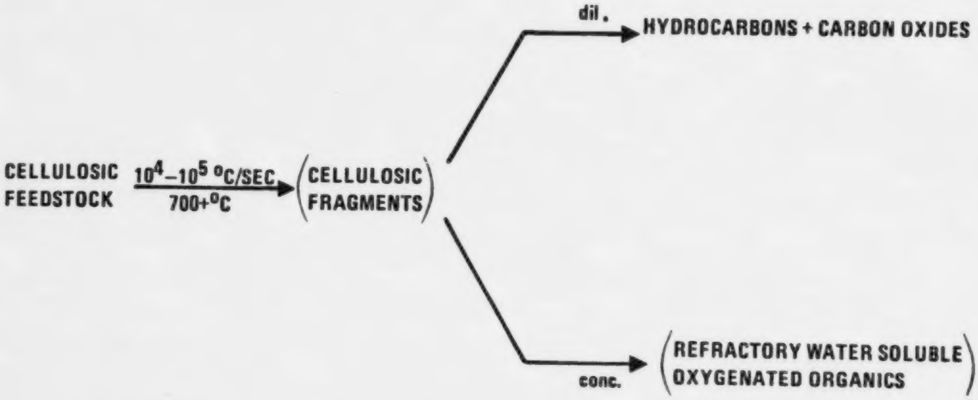

dil.
HYDROCARBONS + CARBON OXIDES
CELLULOSIC FEEDSTOCK
10⁴–10⁵ °C/SEC
700+°C
CELLULOSIC FRAGMENTS
REFRACTORY WATER SOLUBLE OXYGENATED ORGANICS
conc.

Figure 21. High-Temperature Pyrolysis Reaction Overview.

The dilution of the pyrolysis reaction also apparently has another very important effect. Returning to Figures 21 and 22, it is thought that the primary reaction competing with the gasification is a second-order reaction (bimolecular) involving the oxygenated, primordial, free radicals. It is postulated that, if these oxygenated free radicals collide and react with each other, stable oxygenated compounds would result which could be of a refractory nature and survive the high temperature exposure. In order to maintain the elemental balance, these refractory organic compounds would need to be highly oxygenated.

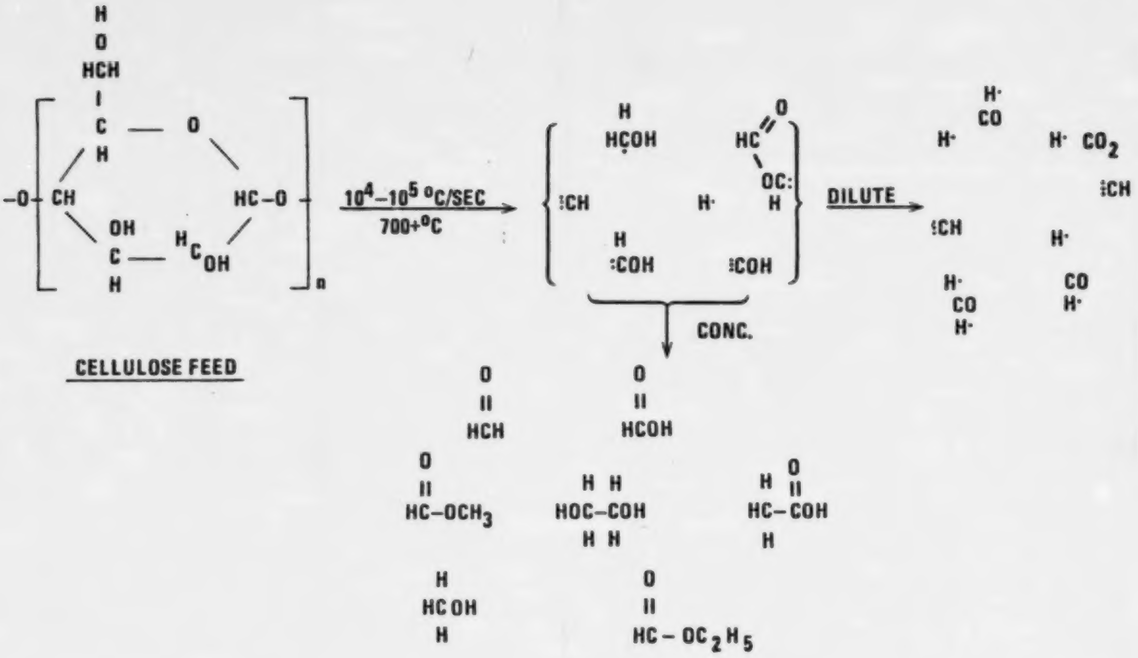

CELLULOSE FEED
10^4–10^5 °C/SEC
700+°C
DILUTE
CONC.

Figure 22. Competing High-Temperature Pyrolysis Reaction Details.

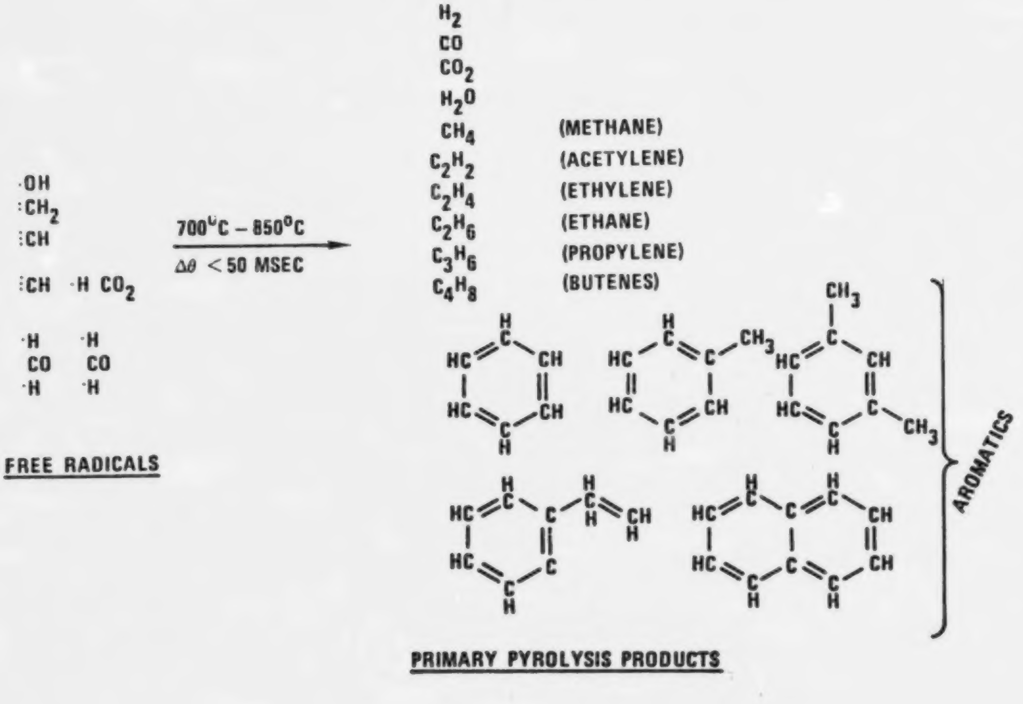

FREE RADICALS
700°C – 850°C
Δθ < 50 MSEC
H_2
CO
CO_2
H_2O
CH_4 (METHANE)
C_2H_2 (ACETYLENE)
C_2H_4 (ETHYLENE)
C_2H_6 (ETHANE)
C_3H_6 (PROPYLENE)
C_4H_8 (BUTENES)
AROMATICS
PRIMARY PYROLYSIS PRODUCTS

Figure 23. Formation of Primary Pyrolysis Products.

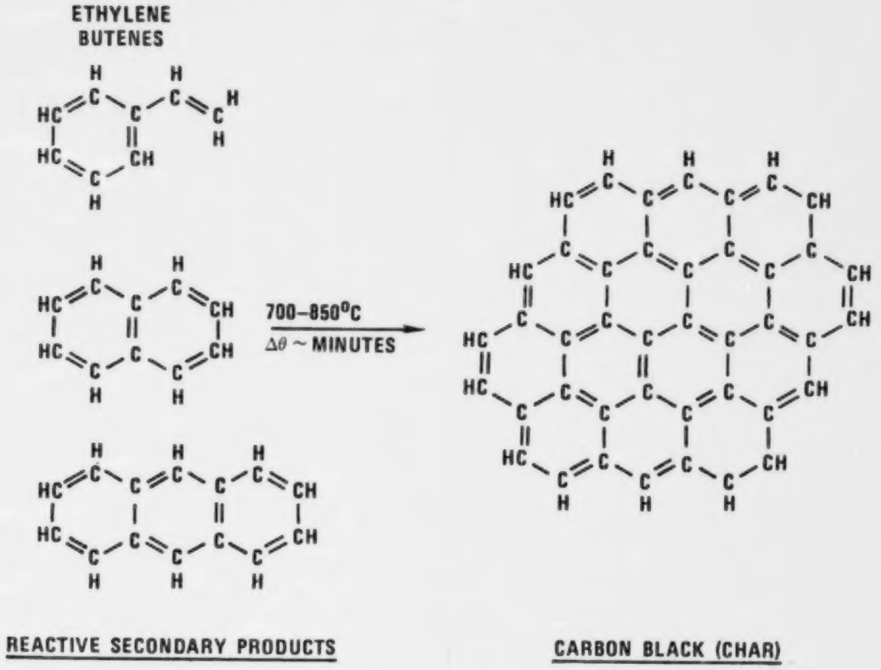

ETHYLENE
BUTENES
700–850°C
Δθ ~ MINUTES
REACTIVE SECONDARY PRODUCTS
CARBON BLACK (CHAR)

Figure 24. Formation of Secondary Pyrolysis Products.

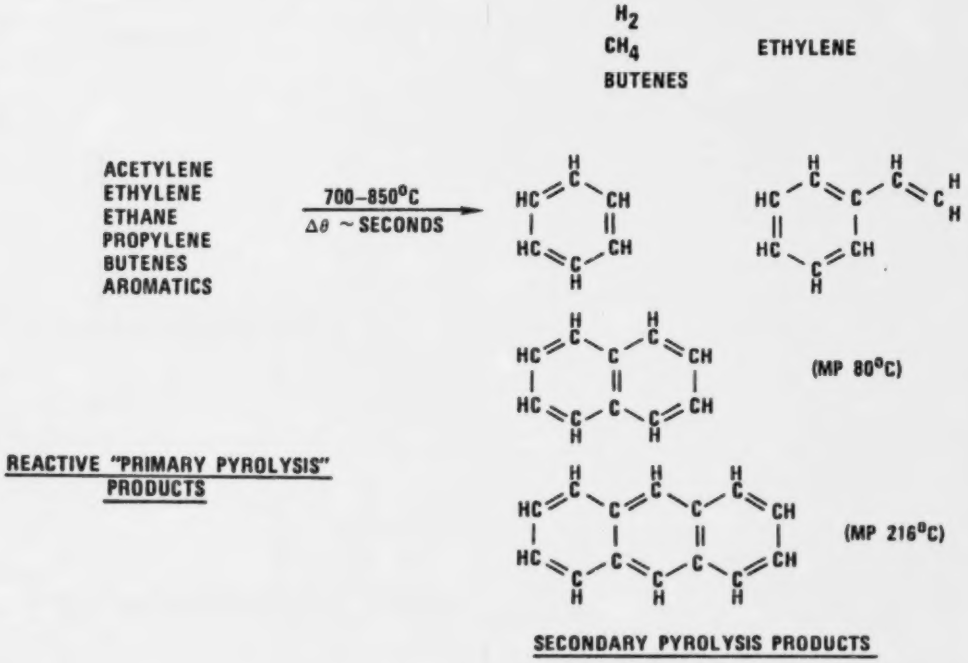

H2
CH4
BUTENES
ETHYLENE
ACETYLENE
ETHYLENE
ETHANE
PROPYLENE
BUTENES
AROMATICS
700–850°C
Δθ ~ SECONDS
(MP 80°C)
(MP 216°C)
REACTIVE "PRIMARY PYROLYSIS" PRODUCTS
SECONDARY PYROLYSIS PRODUCTS

Figure 25. Formation of Carbon Black.

If it is assumed that ignition of a compound involves the combustion of the products of decomposition, then the question of relative thermal stability can be qualitatively compared by consideration of the autoignition temperature of that compound. Table 6 is a compilation of autoignition temperatures taken from the literature.(34)(35) Since autoignition data show quite a spread in the reported values for the same compound, probably only values differing by more than 25°C are significantly different. It is interesting to note that there are indeed many oxygenated compounds which have autoignition temperatures (thermal stabilities) equal to or higher than that of ethylene. These thermally stable compounds include phenols, triethylene glycol dimethyl ether, formic acid, ethyl formate, and acetic acid. Between the stability of ethylene and propylene are acetone, methyl ethyl ketone, and methyl acetate. These oxygenated compounds tend to have a fairly high solubility in water. This solubility tends to allow them to be relatively unnoticed in the aqueous phase of the pyrolysis condensates and helps to explain the lack of closure of the mass balance for most of the pyrolysis experiments which have low gasification.

The qualitative agreement of the autoignition value with relative thermal stability can be illustrated with the compounds acetone and acetaldehyde. Acetone has an autoignition temperature of 538°C, whereas the value for acetaldehyde is only 185°C. At 750°C the half-life of acetone is calculated to be 0.290 second,(38) whereas the half-life of acetaldehyde is only 0.006 second,(39) which is a ratio of almost 50. Interestingly enough, the reported acetone decomposition products for short pyrolysis times had nearly the same ratio of ethylene to carbon monoxide as noted herein for ECO II feedstock, although the acetaldehyde decomposed to give only methane and carbon monoxide.

It is doubtful that the oxygenated organics formation could be explained by a mechanism involving incomplete pyrolysis because the gasification reaction to olefins did not appear to be very dependent on cracking severity; e.g., residence time and temperature. If the oxygenated, water-soluble compounds were products of unimolecular degradation, the relative dilution should have had no effect on yields and the more severe pyrolysis reactions would have been expected to increase the overall gasification, but these trends were not observed. It should be noted that the hypothesis for pyrolysis in the entrained bed reactor is based only on experiments using ECO II as feedstock. Pure cellulosic feedstock or biomass feedstocks may behave differently when pyrolyzed in this manner.

For a discrete particle of organic feedstock to undergo the selective gasification, a very rapid heating rate appears to be necessary. Referring to Table 4, many of the residence times were in the neighborhood of 0.050 second. The temperature rise was from 25°C to about 750°C during pyrolysis. This results in a heating rate of at least 14,500°C/sec. If the particle were to attain the pyrolysis temperature part way through the pyrolysis reactor, the heating rate would be much higher.

A very high heating rate is needed to minimize the time during which the particle is acted upon by competing reactions which do not form the desired olefin-containing products.

TABLE 6. AUTOIGNITION TEMPERATURES AND SOLUBILITY DATA FOR SELECTED COMPOUNDS

Compound	Empirical formula	Room temperature phase	Autoignition temperature, °C (35) (36)	Solubility, parts in 100 parts water (37)
Phenol	C_6H_6O	L	715	∞ (hot)
Carbon monoxide	CO	G	651	slight
Triethylene glycol	$C_8H_{18}O_4$	L	631	?
m-Cresol	$C_6H_6O_2$	L	626	0.5
Formic acid	CH_2O_2	L	601	∞
Hydrogen	H_2	G	585	slight
Ethyl formate	$C_3H_6O_2$	L	577	11
Methyl phenyl ketone	C_8H_8O	L	570	insol.
Ethylene oxide	C_2H_4O	L	570	∞
Acetic acid	$C_2H_4O_2$	L	566	∞
Toluene	C_7H_8	L	552	insol.
Ethylene	C_2H_4	G	543	slight
Methane	CH_4	G	538	slight
Benzene	C_6H_6	L	538	0.07
Acetone	C_3H_6O	L	538	∞
Methyl ethyl ketone	C_4H_8O	L	516	37
Ethane	C_2H_6	G	510	slight
Methyl acetate	$C_3H_6O_2$	L	502	33
Propylene	C_3H_6	G	497	slight
Ethyl acetate	$C_4H_8O_2$	L	482	8.5
Propionic acid	$C_3H_6O_2$	L	475	∞
Methanol	CH_4O	L	470	∞
Propyl acetate	$C_5H_{10}O_2$		460	1.6
Propane	C_3H_8	G	468	6.5
Methyl formate	$C_2H_4O_2$	L	449	30
Tartaric acid	$C_4H_6O_6$	S	428	120
Acrylic acid	$C_3H_4O_2$	L	438	∞
Formaldehyde	CH_2O	G	430	very sol.
Vinyl acetate	$C_4H_6O_2$		427	2
Propylene glycol	$C_3H_8O_2$	L	421	∞
Ethylene glycol	$C_2H_6O_2$	L	413	∞
Ethyl alcohol	C_2H_6O	L	426	∞
Glycerol	$C_3H_8O_3$	L	393	∞
Allyl alcohol	C_3H_6O	L	378	∞
Dimethyl ether	C_2H_6O	G	350	7.6
Acetylene	C_2H_2	G	335	0.1
Acrolein	C_3H_4O	L	300	40
Acetaldehyde	C_2H_4O	L	185	∞
Ethyl ether	$C_4H_{10}O$	L	180	7.5

In order to achieve this high heating rate, the following are necessary: (1) the surface-to-volume ratio of the feed must be high; (2) the thickness of the particle must be relatively low to reduce the thermal gradient in the particle; and (3) the rate of heat transfer into the particle surface must be very high. The first two requirements can be met with a very small particle size, and/or a "two-dimensional" particle (paper), and/or a "one-dimensional" particle (fiber). The heat-transfer requirement needed for a good gasification is a function of the reactor design and apparently can be met with pure radiation,(14) or with fluidized beds(10) and entrained flow reactors which combine radiation, conduction, and convection.(26) The pyrolysis reactor developed in this program is of the entrained flow design.

The molecular fragments of free radicals formed by the shattering of the cellulosic molecules are small enough that their cellulosic identities are lost in the process. This implies that the free radicals will react to form a product distribution, with the ancestral origins or feedstock being of secondary importance, since the water and carbon oxides are relatively inert. Thus, it would be expected that the relative hydrocarbon product distribution would have similar trends whether the free radicals were made from cellulosic, hydrocarbon, or kerogen (shale oil) feedstocks. The weight percent conversions will, of course, have a direct correlation with feedstock characteristics. As shown in Figure 26, the pyrolysis product distribution obtained from naphtha(25) and oil shale(26) and that from MSW (ECO II) are indeed remarkably similar considering the very different nature of the feedstocks.

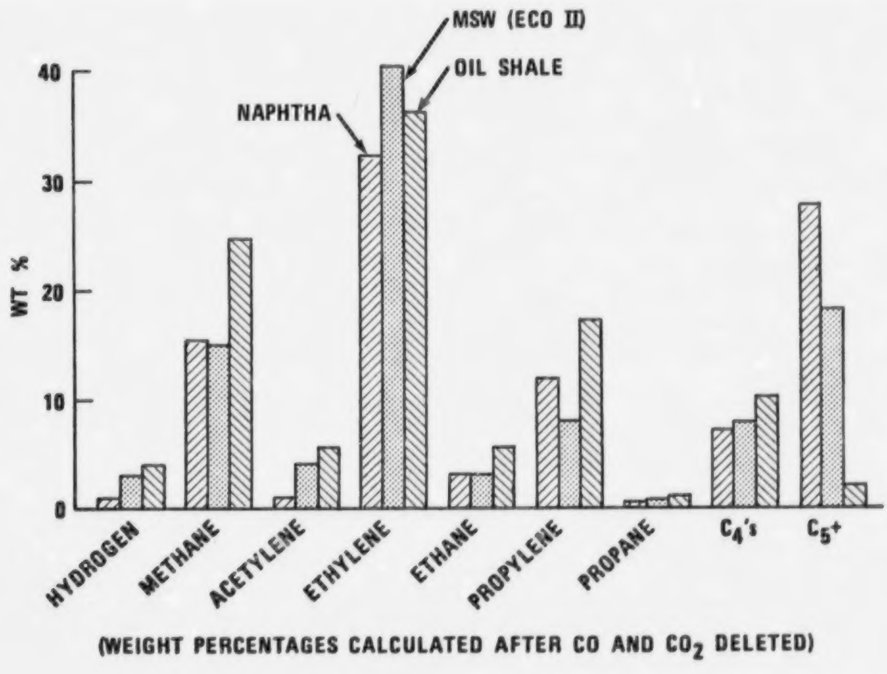


Figure 26. Pyrolysis Products Comparisons Using Various Feedstocks.

In summary, when the cellulosic molecule is rapidly heated to the 700°C temperature regime, very reactive free radicals are formed. These free radicals are very short lived and form the more stable primary pyrolysis products. If the system is relatively dilute (low free-radical partial pressure), the formation of oxygenated organics is not favored. If the pyrolysis reaction is not stopped or quenched, the primary reaction products themselves react to form aromatic tars. With more time, the molecular weight of the tars increases so that they are solid in nature to become carbon black. At this point thermodynamic equilibrium is being approached, and the products are those of the coking ovens: hydrogen, carbon monoxide, char, water, carbon dioxide, and methane. To maximize gaseous hydrocarbon production (e.g., ethylene) it appears necessary to have:

1. A very rapid heating rate to the 700°C temperature regime to form free radicals rather than a slow dehydration reaction to form char, water, and carbon dioxide.

2. A pyrolysis environment which keeps the free radical partial pressure low enough to prevent the free radicals from reacting to form oxygenated products and/or tars.

3. A relatively short gaseous residence time to prevent the formation of secondary reaction products.

The analogy of this hypothesis to that widely accepted for hydrocarbon pyrolysis appears to be very close. Apparently, if one wants to make gaseous hydrocarbons, such as ethylene, from organic wastes, a technology transfer from the petrochemical industry to solid-waste management is in order. The intent of this program has been to help effect this technology transfer.

SECTION 5

HIGH-PRESSURE GAS PURIFICATION

BACKGROUND

The goal of the gas purification portion of the proposed process was to separate the hydrogen sulfide, carbon dioxide, carbon monoxide, hydrogen, and methane from the pyrolysis gases. This would provide a gas stream to the polymerizer consisting primarily of low-molecular-weight olefins; e.g., ethylene, propylene, and butylene. Since the polymerizer reactor is operated at elevated pressures, it was assumed that the pyrolysis gases would be compressed to some intermediate pressure for purification. The effect of hydrogen sulfide in the purified gas stream fed to the polymerizer would be to form odiferous mercaptans which would condense in the gasoline product.(40) The presence of methane or hydrogen in the purified gases would reduce the effective pressure and slow the polymerization reaction.(19) Gas purification can be accomplished at cryogenic temperatures by distillation techniques. However, it was reported to be more energy efficient to use solubility differences of the gases at ambient or elevated temperatures and pressures. The absorption of low-molecular-weight olefins into a light oil from gases formed by the pyrolysis of propane has been commercialized, and ethylene recoveries of 99% have been reported.(41) These propane pyrolysis gases were very similar in general composition to those made from cellulosic pyrolysis except for the oxides of carbon found with the latter.

No data were found to predict the absorption of carbon monoxide into hydrocarbons. Because of its very low boiling point (-192°C), carbon monoxide would probably be absorbed more than hydrogen (boiling point = -253°C) and less than methane (boiling point = -161.49°C). Since the oil absorption approach reportedly would reject both hydrogen and methane, it probably would also satisfactorily reject carbon monoxide. This assumption seemed reasonable, since the commercial processes utilized to remove carbon monoxide from hydrogen involve a catalytic conversion to carbon dioxide for subsequent removal rather than a technique involving direct absorption into oil.(42)

Calculations to predict the solubility of carbon dioxide in hydrocarbon oils indicated that significant quantities of this gas would probably be absorbed along with the desired ethylene. Hence, the carbon dioxide would have to be removed from the pyrolysis gas stream ahead of the hydrocarbon absorption column. Common methods of removing carbon dioxide at elevated pressure include absorption by water, organic amines, or potassium carbonate solutions. The commercial use of water to purify mixtures of hydrogen, carbon monoxide, and carbon dioxide was used for making methanol(43) and also for ammonia synthesis.(44) The absorption of carbon dioxide with water was initially chosen for the purification system due to its inherent simplicity, a lack of heat exchangers, and the relatively low energy requirements (if power is recovered from the high-pressure "rich" water).

EXPERIMENTAL

Initial Flow Sheet

The initial gas purification flow sheet was that shown in Figure 27. As is shown, the raw pyrolysis gases entered the compressor where they were compressed to pressures between 3100 and 9300 kPa (450 - 1350 psi) for storage in a surge tank. From the surge tank the gases flowed through a forward pressure regulator into the bottom of the carbon dioxide scrubber at 3100 kPa (450 psi). The carbon dioxide and hydrogen sulfide were absorbed by water flowing downward countercurrently to the upward flowing gases. The water was pumped by a nonadjustable piston pump. The gas-rich water accumulated in the bottom of the scrubber until it activated the liquid-level controller which opened the solenoid valve to dump the water. This gas-rich water was depressurized, degassed, and recycled, or dumped into the drain. The gases then flowed into the hydrocarbon absorber about one-third up from the bottom. The desired olefins were absorbed in the countercurrently flowing absorber oil (benzene). The bottom of the absorber was maintained at 120°C to boil off absorbed methane, hydrogen, and carbon monoxide from the rich oil. Hydrogen, carbon monoxide, and methane exited the top of the hydrocarbon absorber column as a "medium Btu" gas stream suitable for use by stationary internal combustion engines or as a furnace fuel. The rich oil accumulated in the bottom of the absorber until it activated the liquid-level controller. This controller opened the solenoid valve, allowing the rich oil to pass into the hydrocarbon stripper column about one-third up from the bottom. The bottom of the stripper column was held near the boiling point of the absorber oil (about 230°C at 3000 kPa) which drove the lower boiling hydrocarbons up to the top of the stripper column. The hydrocarbons in the pyrolysis gas stream, which have a boiling temperature the same as or higher than the absorber oil, accumulate in the lean oil storage tank.

This hydrocarbon absorbing and stripping system has been commercialized for the recovery of ethylene and propylene from the gases formed in the pyrolysis of hydrocarbons. The absorber oil was initially circulated with a gear pump.

Equipment

All high-pressure tubing was 0.64-centimeter (1/4-inch) 316 stainless steel tubing. The stainless steel tube fittings were of the single ferrule compression type. Stainless steel tubing interconnected the control room and the purification and polymerization systems. To ensure personnel safety, the systems were installed 15 to 30 feet away from the control room behind a thick earth-filled concrete barricade. All high-pressure tubing was secured with heavy duty tube clamps which served to dampen vibrations and to secure the lines in the event of mechanical failure. Figures 28 and 29 show two views of the purification and polymerization systems.

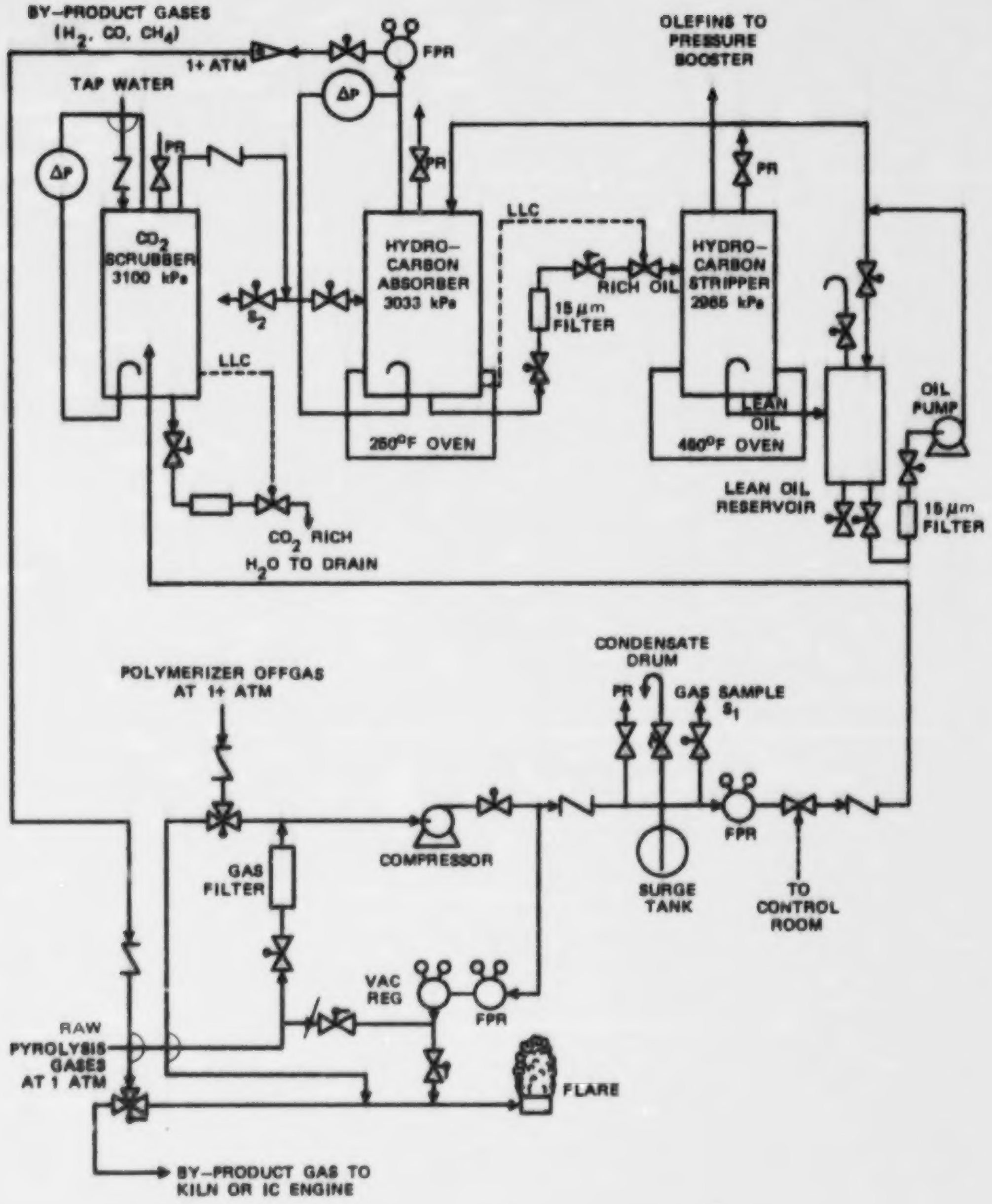

BY-PRODUCT GASES
(H2, CO, CH4)
1+ ATM
FPR
OLEFINS TO
PRESSURE
BOOSTER
TAP WATER
ΔP
ΔP
PR
PR
PR
CO2
SCRUBBER
3100 kPa
HYDRO-
CARBON
ABSORBER
3033 kPa
LLC
HYDRO-
CARBON
STRIPPER
2965 kPa
RICH OIL
15 µm
FILTER
S2
LLC
250°F OVEN
LEAN
OIL
460°F OVEN
OIL
PUMP
LEAN OIL
RESERVOIR
15 µm
FILTER
CO2 RICH
H2O TO DRAIN
CONDENSATE
DRUM
POLYMERIZER OFFGAS
AT 1+ ATM
PR
GAS SAMPLE
S1
COMPRESSOR
FPR
SURGE
TANK
TO
CONTROL
ROOM
GAS
FILTER
VAC
REG
FPR
RAW
PYROLYSIS
GASES
AT 1 ATM
FLARE
BY-PRODUCT GAS TO
KILN OR IC ENGINE

Figure 27. Initial Gas Purification Flow Chart.

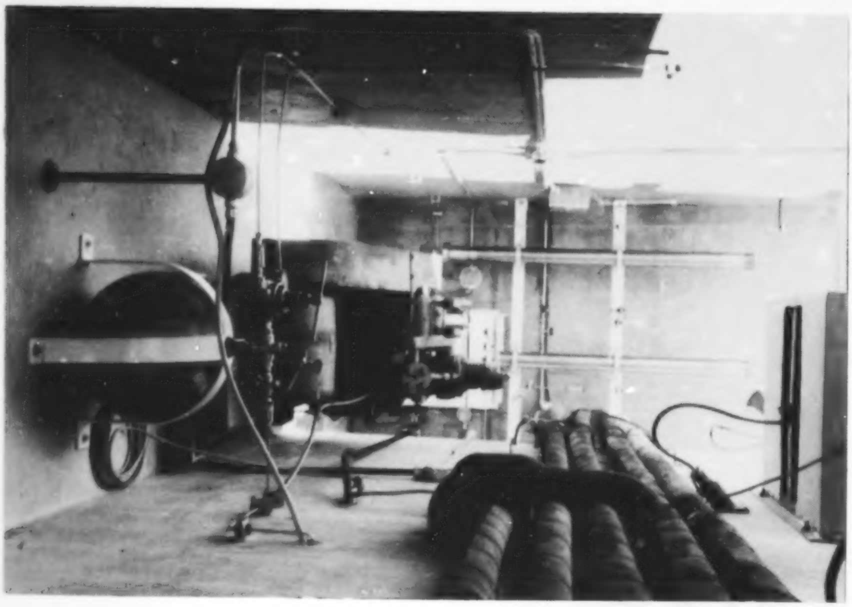


Figure 28. Pyrolysis Gas Compression, Storage, and Purification Equipment.

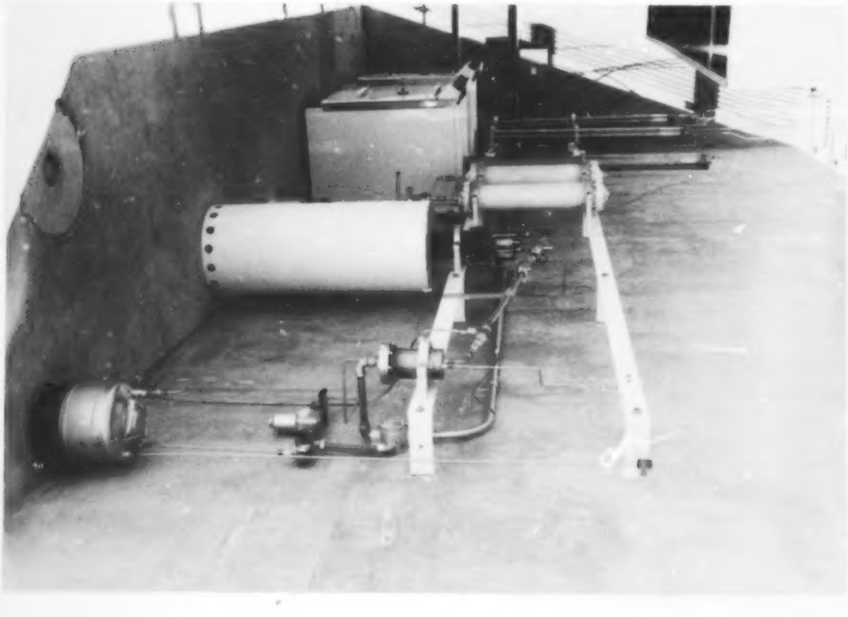


Figure 29. Pyrolysis Gas Purification, Pressure Boosting, Polymerization, and Gasoline Storage Equipment.

In the foreground of Figure 28 is the 34-liter (9-gallon) spherical pyrolysis gas storage or surge tank. The three-stage compressor is immediately behind the storage tank. In the background are the carbon-dioxide scrubber column on the left and the hydrocarbon absorber column on the right. The lower end of the hydrocarbon absorber is inside of a gas-fired oven used to maintain the rich oil at 121°C (250°F).

The scrubber column, as well as the absorber and stripper columns, was fabricated from 304 stainless steel schedule 80 "3-inch" pipe having an outside diameter of 8.9 centimeters with a wall thickness of 0.78 centimeter. The overall length of the scrubber was 169 centimeters (5 1/2 feet). The columns were packed with about 145 centimeters of 0.6-centimeter (1/4-inch) ceramic saddles.

In the background of Figure 29 are seen the same scrubber and absorber shown in Figure 28. In front of the hydrocarbon absorber is the stripper column, which is placed in a high-temperature gas oven in order to boil or strip off the desired olefins from the oil. The two identical short tanks in front of the stoves are the pressure booster tanks that compress the olefins from 2975 to 5175 kPa (430 psi to 750 psi), using compressed nitrogen.

The pumps and solenoid valves were remote controlled from the control room. All electric circuits that are part of the purification and polymerization systems had individual lights on the control panel to indicate when the pumps were running and when the solenoids were actuated.

The control panel was designed so that the electrical and pneumatic controls were superimposed on a simplified flow diagram similar in form to the flow diagram shown in the control panel of Figure 30. The flow lines were color coded for ease of interpretation. During the operation of the system, the importance of the descriptive control panel was very evident as it was helpful in minimizing operator errors. Figure 30 shows this control panel.

To monitor the high-pressure systems, 15 thermocouple channels were added. These 15 channels were connected to a multipoint recorder which could be set to record as many of the channels as desired. One of the channels was also connected to the temperature recorder-controller that controlled the polymerizer-reactor heater.

Test Results

The coupling of the low-pressure pyrolysis system to the high-pressure purification system with the available, but oversized, compressor required that some experience be gained. In run 51, the compressor was allowed to operate for 10 minutes, but the pyrolysis feeder head plugged. Unplugging the feeder head resulted in the system temporarily passing air to the compressor and, consequently, to an unacceptable level of air in the stored gases. The surge or storage tank was then depressurized to allow the potentially explosive gases to escape.

Run 52 was relatively more successful, and the surge tank was pumped up to 4900 kPa (700 psig). The stored gas had substantially the same composition

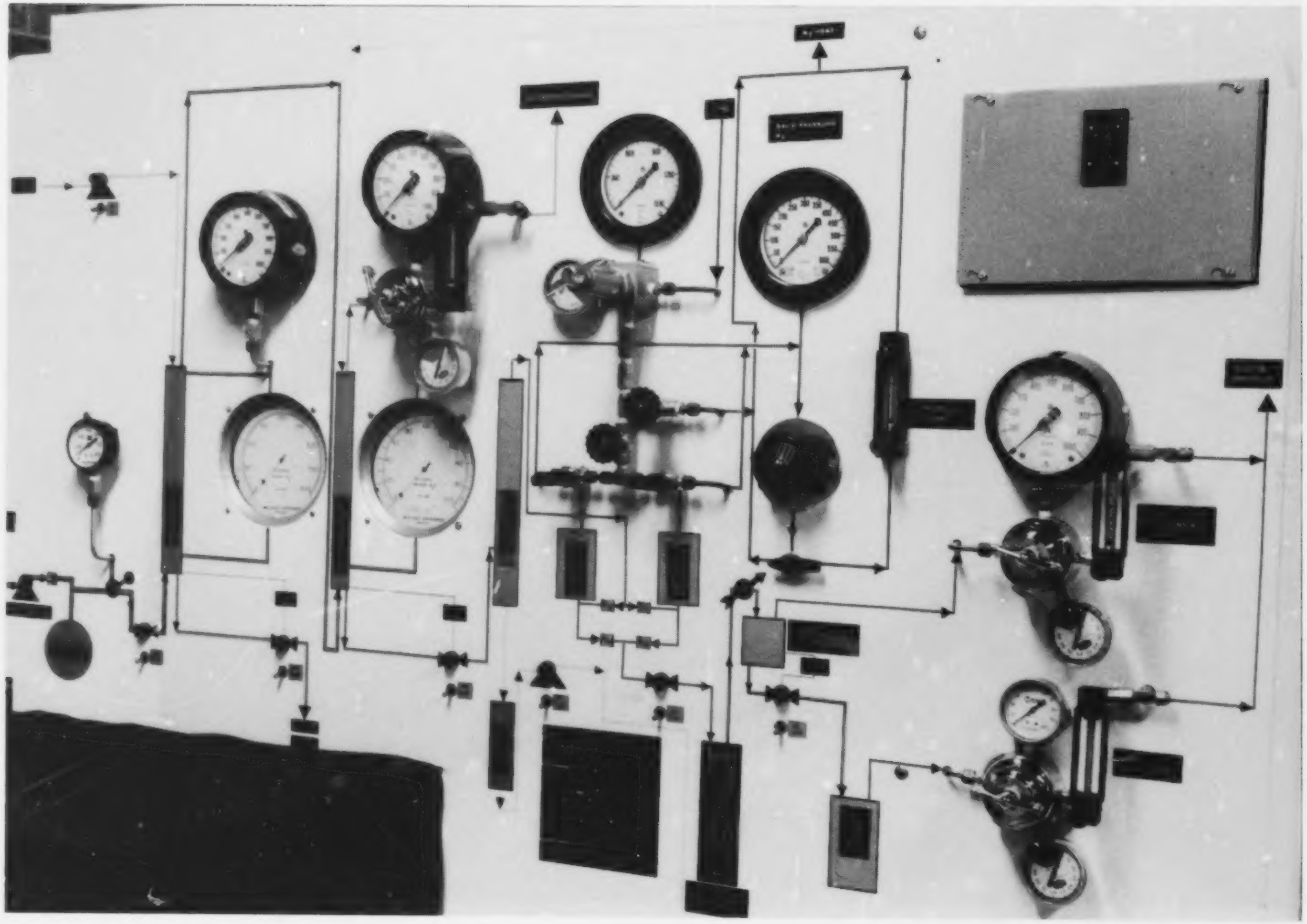


Figure 30. Control Panel for Pyrolysis Gas Conversion to Gasoline.

as a sample taken during the run from the low-pressure system. Unfortunately, the Buna-N O-ring in the check valve located at the surge tank inlet was so badly swollen by the condensates at the end of this run that it would not seal. Virtually all of the stored gas bled into the flare and was lost. The check valve was replaced with one having a Teflon seal to successfully solve this problem. Experimentation with a Viton O-ring in the compressor condensates indicated that it would also swell and be unserviceable.

In run 53, about one-third of the gases compressed and stored was air, due to difficulties with the operation of the pyrolysis system. It was allowed to bleed off.

Run 54 was an improvement with a surge tank pressure of 4500 kPa (640 psig), although the stored gases contained 9% air. The stored gas was passed to the carbon dioxide scrubbing column where it was washed and sampled. The air in the semienclosed water drain was also sampled. As can be seen from Table 7 the scrubber product had the carbon dioxide content reduced to from 30% to 0.56%, but the rejected gas appeared to have a large quantity of unsaturated gases, hydrogen, and carbon monoxide in it. The removal (loss) of desirable gases was attributed to the overwashing during the transient operating conditions. The presence of combustible gases in the drain led to the installation of a long tube away from the building to vent the potentially combustible gases.

Run 55 resulted in a surge tank pressure of 5600 kPa (800 psig). These pyrolysis gases were used to further pressurize the purification system and check out the equipment. The carbon dioxide scrubber product gases were checked and found to have only about 1% carbon dioxide content whereas the pyrolysis gases contained 41% by volume. The scrubber reject stream contained about 75% carbon dioxide, but also about 11% by volume C_2+ material. The hydrocarbon absorbing-stripping section checkout was begun, but since the system had been prepressurized with nitrogen, no conclusive results could be drawn.

Run 56 pyrolysis gases were used to continue the checkout of the purification system. The water pump selected had only one speed and stroke, but some flow control was obtained by the use of a metering valve to bypass excess flow. During this run, the water flow was minimized, and a relatively high by-product gas flow was used in an effort to minimize the loss of desirable gases into the water. The scrubber product gas contained only about 1% carbon dioxide compared with the 31 1/2% in the pyrolysis gases. The original lean oil pump was a gear pump using Teflon gears and was capable of developing only about 175 kPa (25 psig) differential pressure before decoupling from the magnetic drive. Unfortunately, the lean absorber oil (mostly benzene) was too low in viscosity and resulted in the gear pump performing more like a centrifugal pump. The oil flow was therefore a function of the pressure difference between the hydrocarbon stripper and absorber, and the total pressure was nearly 20 times the differential pressure. This led to a varied oil flow rate which qualitatively was monitored by the cyclic rate of the hydrocarbon absorber's liquid-level controller. Part of the problem with the varied oil flow was the difficulty of maintaining the desired temperature.

TABLE 7. RUN 54 GAS CHROMATOGRAPH DATA (PERCENT BY VOLUME)

	Pyrolysis surge tank	Transient CO_2 scrubber product	"Air" from drain	Rejected gas in drain
Hydrogen, H_2	8.1	15.17	1.08	8.59
H_2S	0	0	0	0
Propane	0.09	0.19	0	0
Propylene	2.02	2.93	0.22	1.75
Isobutane	0.09	0	0.01	0.08
n-Butane	0	0.01	0	0
l-Butene	0.34	0.61	0.02	0.16
Isobutene	0	0	0	0
Trans-Butene-2	1.09	0.52	0.10	0.79
cis-Butene	0.03	0.02	0	0
Isopentane	0	0	0	0
n-Pentane	0.11	0	0	0
CO_2	30.49	0.56	4.4	34.98
C_2H_4	8.39	10.53	1.31	10.41
C_2H_6	0.61	1.23	0.09	0.72
C_2H_2	1.01	0	0.20	1.59
O_2	1.29	0	18.55	0
N_2	7.84	0	68.87	0
CH_4	6.89	11.39	1.06	8.43
CO	28.18	56.57	3.99	31.72
$C_5^{=} + C_6{+}$	3.44	0.25	0.09	0.72

The pyrolysis portion of run 57 produced a surge tank pressure of 6900 kPa (995 psig). This gas was utilized to determine if the flow from the gear pump could be stabilized sufficiently to be useful. Problems were encountered which indicated that the gear pump would not be likely to produce the constant flow required. Aluminum fins had been bolted onto the bottom of both the absorber and the stripper to act as heat sinks to moderate the temperature fluctuations and to improve heat transfer into the columns. In addition, a 6-meter (20-foot) length of 0.6-centimeter (1/4-inch) stainless steel tubing was coiled and placed in the stripper oven to preheat the rich oil. After this run, it was concluded that the gear pump would have to be replaced with a piston metering pump having an adjustable flow rate (stroke). The nitrogen bleed gas from the pressure booster was analyzed and found to have no contamination from the boosted gases. The accumulated gases in the boosters were compressed to 5175 kPa (750 psig), passed through the cold polymerizer, and flared off.

It was pointed out by the (Dow) consultant that chlorine compounds such as aluminum chloride are known calalysts for olefin polymerization and that the use of tap water for carbon dioxide scrubbing was unnecessarily introducing chlorine into the system. It was decided to add the capability of recycling the scrubbing water while the system was waiting for the new lean oil pump to arrive. A 49-liter (13-gallon) stainless steel drum was mounted on top of the barricade inside of a well-insulated double-wall plywood box to prevent freezing. The rich water was depressurized to atmospheric pressure into the drum. This caused the dissolved gases to come out of solution as the two phases entered the drum in a circumferential tube.

Run 58 was the first purification run with the piston metering pump for the lean oil and with the scrubber water recycle. The new lean oil piston metering pump worked very well and proved to be trouble-free during the program. The Teflon packing around the piston held up very well. The water recirculation system for the carbon dioxide scrubber mechanically functioned well. The gas analyses made for this run are shown in Table 8. As can be seen, the rejected carbon dioxide stream still had 19% by volume of combustible gases in it, and 12% was the desirable hydrocarbons. The by-product fuel gas stream had only 0.9% carbon dioxide, but an undesirably high 1.7% ethylene. The hydrocarbon stripper product gas contained only 27.5% of the desired hydrocarbons and was contaminated with 5% hydrogen, 17% carbon dioxide, 17% methane, and 34% carbon monoxide.

TABLE 8. PURIFICATION RUN 58 GAS DATA (PERCENT BY VOLUME)

	Surge tank	Rejected CO_2 (1600 hr)	CO_2 scrubber product (final)	Initial stripper product (without N_2)	Final stripper gas, (without N_2)	By-product gas (1500 hr)
Hydrogen, H_2	10.3	1.0	13.2	5.8	5.4	24.1
H_2S	...	...	...	...	...	...
Propane	0.1	...	tr	...	0.2	...
Propylene	1.7	0.8	1.2	1.3	2.8	0.2
Isobutane	0.1	0.1	tr	...	tr	...
n-Butane	tr	0.1	...	...	...	...
I-Butene	0.1	0.1	tr	0.1	0.1	...
Isobutene	...	...	...	...	...	...
Trans-Butene-2	0.5	0.8	0.1	0.1	0.2	...
cis-Butene	tr	...	...	...	...	...
Isopentane	...	...	...	...	...	...
n-Pentane	tr	0.1	...	...	...	...
CO_2	31.4	81.1	12.6	4.9	17.1	0.9
C_2H_4	8.5	6.8	10.8	12.3	21.2	1.7
C_2H_6	0.1	0.2	1.0	1.4	2.3	0.2
C_2H_2	0.1	2.9	0.2	...	0.3	...
O_2	0.2	0.1	...	0.5	...	0.3
N_2	2.3	0.4	2.6	0	0	0
(actual N_2, %)				(74.08)	(40.51)	(20.8)
CH_4	8.9	1.3	12.7	26.3	16.6	8.9
CO	34.5	3.9	45.4	47.4	33.5	64.6
$C_5^{=} + C_6 +$	0.1	0.4	0.3	...	0.4	0.4
H_2/C_2H_4	1.2	0.1	1.2	0.5	0.2	14.2
CH_4/C_2H_4	1.0	0.2	1.2	2.1	0.8	5.2
CO_2/C_2H_4	3.7	11.9	1.2	0.4	0.8	0.5

At this point it was strongly suspected that although high-pressure water washing was used by the Germans in World War II to scrub carbon dioxide from synthesis gases for the Fischer-Tropsch process, this form of gas purification was unsuitable for the case where significant amounts of olefins and acetylene were present. To verify this conclusion, calculations were made using Henry's Law which states that the relative amount of a gas dissolved in a liquid is proportional to the partial pressure of that gas above the liquid, although this law is usually recommended for use at low partial pressures. Using the raw pyrolysis gas composition, the expected "carbon dioxide reject" composition was calculated. The ratios of the actual to the calculated volume percentages were as follows: 1.4 for hydrogen, 1.3 for methane, 0.83 for acetylene, 1.9 for ethylene, 0.58 for propylene, 1.6 for carbon monoxide, and 0.93 for carbon dioxide. These results verified that significant amounts of olefins and by-product fuel gases could be expected in the carbon dioxide reject stream and that their presence did not necessarily imply gas bubble entrainment in the "rich", gas-saturated water. It was concluded that high-pressure water washing for carbon dioxide removal was not suitable for the process.

Before the system was shut down to modify the carbon dioxide removal subsystem, it was decided to verify early calculations that the carbon dioxide had to be removed separately. Run 59 was conducted with no water flowing in the carbon dioxide scrubber. Thus raw pyrolysis gases were allowed to pass to the hydrocarbon absorber. Although the by-product fuel gas stream did contain 14% by volume carbon dioxide, the hydrocarbon stripper product gases contained 56% which contributed to the ethylene percentage increasing only from 8% in the pyrolysis gases to 19% in the stripper product. It was concluded that carbon dioxide should be removed in a separate subsystem. Subsequently, solubility data for carbon dioxide in benzene were found.(45) These data verified that carbon dioxide and ethylene have similar solubilities, which requires a removal of carbon dioxide prior to the hydrocarbon absorber. It was decided to go to the hot-carbonate method for carbon dioxide removal.

The hot-carbonate method selected uses a 25% aqueous potassium carbonate solution at 113°C (235°F) to chemically react with the carbon dioxide at 3100 kPa (450 psia) and thus to form the bicarbonate in the carbon dioxide scrubber. The solution is regenerated at near atmospheric pressure with steam stripping and is then recirculated. Although the hydrogen sulfide apparently is absorbed by the condensate in the surge tank in the NWC bench-scale unit, the hot-carbonate solution would also remove hydrogen sulfide from the pyrolysis gases if it were present.(46)

Among the advantages of the hot-carbonate system over other carbon dioxide removal systems, such as monoethanolamine (MEA), are much lower usage of regeneration steam and fewer heat exchangers, since absorption and regeneration occur at nearly the same temperature.(47) Compared with high-pressure water washing, the amount of water circulated is greatly reduced and the solubility of the by-product fuel gases in the carbonate solution is only about one-fifth that in pure water.(42)

The carbon dioxide removal subsystem was modified from the ambient temperature water washing system to the hot-carbonate system. A stripping column was added to the top of the 49-liter (13-gallon) drum. This column was almost identical to the other columns in the purification system, but had a thinner wall. A water-cooled condenser was added to the top of the stripper column to condense the regenerative steam. The carbon dioxide rich solution (actually rich in potassium bicarbonate) entered a few inches below the top of the column and was allowed to flow downward through the packed column countercurrently to the rising regeneration steam. The regenerative steam was made by boiling the carbonate solution in the bottom of the drum with a rheostatically controlled electric hot plate. The carbon dioxide absorber was wrapped with high-temperature heating tapes which were also rheostatically controlled. A stainless steel, dual-piston metering pump system replaced the much larger mild steel pump used for water washing. The system was then well insulated. A 25% by weight aqueous solution of potassium carbonate was added to the stripper drum, and the system was leak tested. A troublesome leak was detected in the scrubber's liquid-level controller pipe joint, which Teflon tape could not seal. An attempt to use a commercial liquid-thread sealant appeared to be surprisingly poor (the only time it didn't work). Finally silicone adhesive was liberally applied to the inside of the joint, and this method proved to work well for the duration of the program. The pressure in the stripper system was maintained using a brass pressure-relief valve set at 128 kPa (5 psig). A water-cooled heat exchanger was added to the top of the absorber to minimize the moisture lost with the scrubbed product gases. Figure 31 shows the hot carbonate flow sheet.

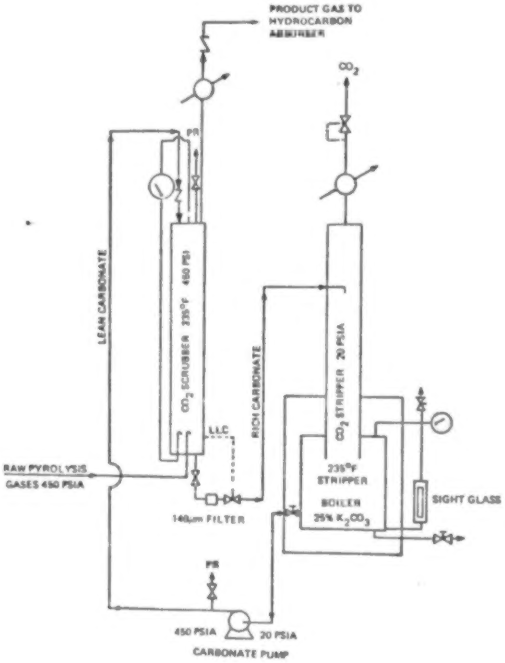

PRODUCT GAS TO HYDROCARBON ABSORBER
CO_2
PR
LEAN CARBONATE
CO_2 SCRUBBER 235°F 450 PSI
RICH CARBONATE
CO_2 STRIPPER 20 PSIA
LLC
RAW PYROLYSIS GASES 450 PSIA
140μm FILTER
235°F STRIPPER
BOILER 25% K_2CO_3
SIGHT GLASS
PR
450 PSIA
20 PSIA
CARBONATE PUMP

Figure 31. Hot Carbonate Flow Sheet.

Numerous problems were encountered in getting the pyrolysis system to again function smoothly. The pyrolysis quench system was replumbed to replace the latex rubber tubing with 0.6-centimeter (1/4-inch) 3.6 stainless steel tubing, and the quench nozzles were enlarged to reduce the probability of plugging. The three-stage compressor valves were contaminated with tars and had to be cleaned.

Run 63 was used for the initial checkout of the new hot-carbonate system. Only qualitative data were generated, which indicated very good removal of carbon dioxide with the product gas having less than 1% carbon dioxide after excessive scrubbing. The hot-carbonate system appeared to work as intended with very few problems.

In runs 60 to 64, the quench water was recycled to the steam boiler to produce the carrier steam. This worked well for the first few runs, but run 64 had problems with the steam system plugging. About 500 grams (wet weight) of precipitated tars and entrained char were removed from the bottom of the quench drum. The tarry material was easily removed by hand. This material was formed from about 16 kilograms of ECO II feed and represented a production of about 3% by weight of tars and entrained char for disposal. The disposal would probably be in the pyrolysis furnace in a scaled-up system. It apparently had been deposited as small tar droplets which had not coalesced into large chunks and which had not wetted the stainless steel drum walls. The material was pliable and could be easily formed into balls at room temperature.

A change in the ECO II to lot T-42 from the depleted lot T-47 resulted in feeding problems, so it was set aside in favor of lot T-52. The feeder head still tended to plug up, so the transport tube was changed from 0.6-centimeter (1/4-inch) to 1.2-centimeter (1/2-inch) tubing. The filter for the compressor was changed to an automotive oil filter system which allowed the use of disposable spin-on filters. The new filter system was first used in run 67 with good results.

Run 69 produced a fully pressurized surge tank which was used to further check the purification system. The liquid level controller contacts in the hydrocarbon absorber were found to stick open if the temperature inadvertently rose much above the desired 120°C (250°F). This would cause the rich oil to accumulate in the bottom of the absorber and require that the system be shut down. It was also found that, when the rich carbonate solution was allowed to cool between tests, the less-soluble bicarbonate would precipitate in the lines and plug the system. Originally the lean oil filter had a 60 μm filter element in it, but this proved to be too fine and would readily plug up. A 140 μm filter element was installed which seemed to protect the pump adequately and did not need to be cleaned very often. Gases sampled from runs 69 and 70 indicated that there was a considerable amount of the by-product fuel gases appearing in the hydrocarbon stripper product gas and that a considerable amount of olefins was being lost in the by-product fuel gas stream. This occurrence was attributed to the difficulty encountered in raising the bottom of the hydrocarbon stripper to the necessary 230°C (450°F).

In contrast, at the end of purification run 70, the composition of the carbon dioxide stripper gas was very pure and contained 99.37% by volume carbon dioxide, 0.09% acetylene, 0.04% oxygen, 0.25% nitrogen, 0.06% methane, 0.12% carbon monoxide, and 0.07% $C_5^{=}$+ material. (The raw pyrolysis gas of run 70 had a carbon dioxide content of 39.3%.) The carbon dioxide stripper was operated at 124°C (255°F). The carbon dioxide absorber was at 104°C (220°F) at the top and 116°C (240°F) at the bottom. The ratio of rejected carbon dioxide to carbonate solution circulated was 0.022 m^3/l (3.0 ft^3/gal) which is in the range indicated in the literature.(42) Tests were not conducted to determine optimum ratios of pyrolysis gas to carbonate solution because the hydrocarbon absorption system needed to be upgraded. It was noted that the condensate which collected in the rejected carbon dioxide system had an odor reminiscent of cinnamon oil (phenyl acrolein). The hot-carbonate system seemed to work very well considering the relatively short absorption and stripping columns, and it may be that the small amount of water-soluble organics that are absorbed from the pyrolysis gases is acting to increase the absorption rates.

At this time, the rich oil passed from the hydrocarbon absorber to a stainless steel tube 0.6 centimeter (1/4 inch) in diameter by 6 meters (20 feet) long. This tube, which was placed in the stripper oven, preheated the rich oil to about 205°C (400°F). At this temperature, approximately half of the vapors being formed would be the oil itself (benzene). Since this benzene would condense higher up in the column and flow downward countercurrently to the upward flowing vapors, it was thought that the benzene might reabsorb enough olefins to prevent good regeneration. The system was modified by removing the coil and insulating the rich oil line. The rich oil inlet was raised about 38 centimeters (15 inches) in the column.

In run 71 it was found that only about 17°C (30°F) was lost by the rich oil as it went from the bottom of the hydrocarbon absorber to the middle of the hydrocarbon stripper. Unfortunately, the loss of the rich oil heating tube reduced the heat transfer to such an extent that only 193°C (380°F) could be attained on the bottom of the stripper rather than the desired 232°C (450°F). This small difference in temperature is critical to the regeneration efficiency because it nearly doubles the vapor pressure of the benzene. (The more benzene vapors, the better the stripping action.)

The ovens that heat the hydrocarbon absorption and stripping columns were modified so that the flue gases vented up alongside of the bottom 38 centimeters (15 inches) of the columns. Also in the stripper oven, heavy aluminum foil was used to direct the hot combustion gases directly to the bottom of the stripper column. Problems were still encountered in run 72 with inadequate temperature in the bottom of the hydrocarbon stripper. The gas orifice in the stripper oven was replaced with a larger one to help increase the gas flow to the oven. The temperature of the hydrocarbon stripper bottom was raised only to about 210°C (410°F) when the absorber oil was circulating in run 73.

The oven thermostat sensor was then moved to a relatively cooler place in the hydrocarbon stripper oven. In run 74, the bottom of the stripper column finally attained the desired temperature while the oil was circulating. The small amount of concentrated olefins collected was used to check out the pressure booster and polymerization systems.

During run 75, an analysis of the by-product gas revealed that the absorber oil was still not being regenerated very well, even though the hydrocarbon stripper bottom was at the supposedly desired 232°C (450°F). Midway during the run, the hydrocarbon stripper pressure was reduced from 3060 kPa (444 psia) to 2545 kPa (369 psia). This lowering of pressure appeared to greatly improve the regeneration of the absorber oil, and resulted in doubling the rate of flow of stripper product gases into the pressure booster tanks. The ethylene content in the by-product gases was reduced from 4% to 1 1/2% by volume (an estimated 90% recovery) by this improved oil regeneration approach. At the end of this run, the hydrocarbon stripper product had achieved a 38% ethylene and a 48% C_2+ content, with the major contaminants being the by-product fuel gases: 4% hydrogen, 16% methane, and 29% carbon monoxide. The average composition of the gases in the pressure booster tanks was not nearly as rich as the end-of-run product, but it was used to further check out the polymerizer, as will be discussed in a later section. These gas analyses are tabulated in Table 9.

The pyrolysis gas surge tank developed a leaky joint in the 2.5-centimeter (1-inch) flare fitting and had to be welded. The boiler tube for the pyrolysis steam began to scale badly enough to plug the steam ejector. Upon disassembly it was found to have developed a leak and was replaced with a 316 stainless steel tube coil 1.91 centimeters (3/4 inch) in diameter by 7.5 meters (24 1/2 feet) long. The volume of the new boiler tube was approximately the same as the old boiler tube and the old steam surge tank. No steam surge tank was used with the new boiler tube. The steam ejector was replaced by one with a smaller orifice (0.16 centimeter (0.0625 inch)). Only distilled water was used in the new boiler tube to make steam. The liquid level controller in the hydrocarbon absorber had been occasionally sticking, so now that a replacement controller was available, it was installed. It was also found that the stripper oven would deliver more heat to the column if the oven door was left ajar so that the thermostat was cooler.

Runs 77 and 78 were both plagued with evidence that the absorber oil was not regenerating properly, both by gas analyses and by a lack of very much hydrocarbon stripper product. It was then recognized that if the level of oil in the bottom of the stripper did not cover the dip leg of the outlet, the vapors in the bottom of the stripper would condense in the heat exchanger located between the stripper and the lean oil pump. These vapors would have a significant amount of olefins in them so that the condensed liquid being pumped would actually be a poorly regenerated absorber oil. The system was replumbed so that the regenerated lean oil from the bottom of the stripper bypassed the oil reservoir, because small changes in the stripper pressure could transfer the oil back and forth between the stripper and the reservoir. Valves were placed so that oil could be bled off to the reservoir or pumped into the system, as shown in Figure 32. A thermocouple was placed in the hydrocarbon stripper 180 degrees from the rich oil inlet to monitor whether the hot vapors were rising to go to the pressure booster as desired or whether they were passing out the bottom of the stripper to the heat exchanger to condense and be recirculated. A thermocouple was also placed at the top of the column to better monitor the system. During this downtime, salt deposits blocked off the pyrolysis gas inlet tube in the carbon dioxide absorber and had to be drilled out. The surge tank pressure regulator developed a crack in its monel diaphragm and had to be replaced. Valves to isolate the regulator were added so that, in the future, the surge tank would not have to be emptied to service the regulator.

TABLE 9. RUN 75 GAS ANALYSES (PERCENT BY VOLUME)

							A	B	
	Surge tank, 800 psi	By-product gas, 10/13/78 (1245 hr)	By-product gas, 10/13/78 (1315 hr)	Hydrocarbon stripper product, end of run, 10/13/78 (1330 hr)	Booster 1, 10/13/78 (1445 hr)	Polymerizer off gas, 10/13/78 (1520 hr)	Booster 2, 10/19/78 (1440 hr)	Polymerizer off gas, 10/19/78 (1515 hr)	B/A
Hydrogen, H_2	11.91	22.13	23.29	4.40	9.79	8.01	6.98	5.62	0.81
H_2S	0	0	0	0	0	0	0	0	0
Propane	0.06	0.01	0.01	0.09	0.06	0.83	0.08	1.20	15
Propylene	1.46	0.79	0.75	3.15	1.89	2.05	0.74	2.44	3.3
Isobutane	0.06	0.02	0.01	0.08	0.06	0.02	0.07	0.04	0.57
n-Butane	0.07	0	0	0.03	0.02	0.46	0.05	0.66	13.2
I-Butene	0.14	0.03	0.05	0.16	0.07	0.30	0.15	0.38	2.5
Isobutene	0	0	0	0	0	0.08	0	0.11	∞
Trans-Butene-2	0.68	0.13	0.16	0.80	0.40	0.12	0.66	0.15	0.23
cis-Butene	0.02	0	0	0.02	0.01	0.07	0.03	0.09	3.0
Isopentane	. . .	0	0	0	0	0.03	0	0.04	∞
n-Pentane	0.05	0	0	0.02	0.02	0.09	0.02	0.10	5.0
CO_2	29.35	0.06	0.04	0.74	0.37	0.55	0.44	0.70	1.59
C_2H_4	8.28	4.23	1.46	38.28	14.80	6.19	24.92	6.57	0.26
C_2H_6	0.69	0.29	0.09	2.34	0.96	2.71	1.70	3.93	2.31
C_2H_2	1.08	0.15	0.07	2.57	1.02	0	1.74	0	0
O_2	0.43	0.31	0.40	0.17	0.15	0.04	0.14	0.06	0.43
N_2	1.93	3.66	4.00	1.12	2.92	3.60	1.82	2.48	1.36
CH_4	7.70	7.69	6.20	16.26	19.19	22.59	18.69	24.33	1.30
CO	35.70	59.98	62.99	28.92	47.79	51.83	41.13	50.52	1.23
$C_5^= + C_6 +$	0.42	0.49	0.48	0.84	0.49	0.46	0.45	0.57	1.27
$C_2 +$	13.01	. . .	3.08	48.38	. . .	. . .	. . .	. . .	. . .

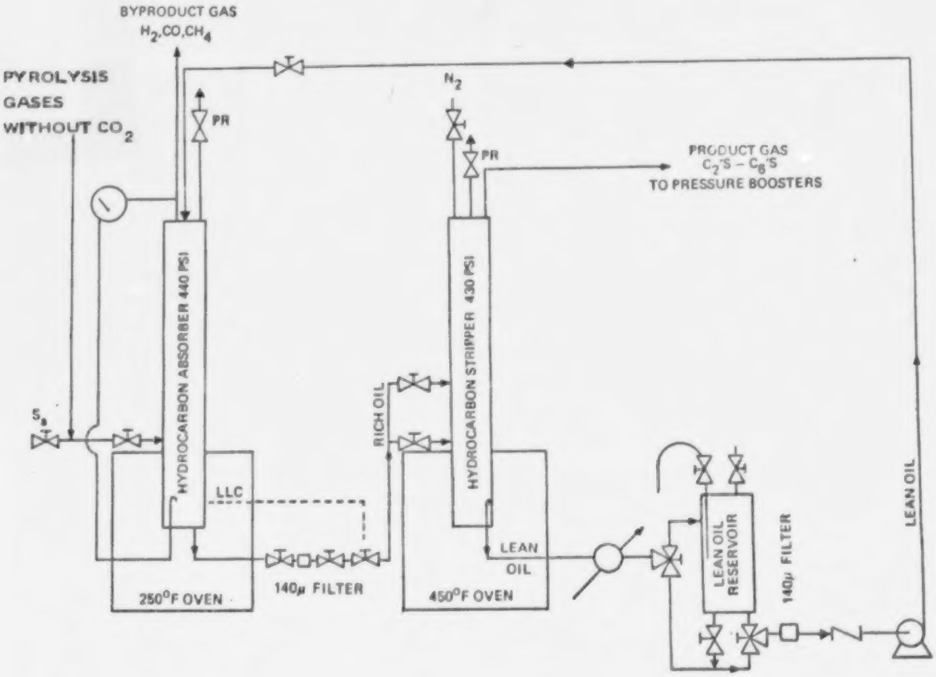

BYPRODUCT GAS
H2,CO,CH4
PYROLYSIS
GASES
WITHOUT CO2
PR
N2
PR
PRODUCT GAS
C2'S – C6'S
TO PRESSURE BOOSTERS
S8
HYDROCARBON ABSORBER 440 PSI
LLC
250°F OVEN
140µ FILTER
RICH OIL
HYDROCARBON STRIPPER 430 PSI
LEAN
OIL
450°F OVEN
LEAN OIL
RESERVOIR
140µ FILTER
LEAN OIL

Figure 32. Final Hydrocarbon Recovery Flow Sheet.

Run 80 served mainly to check out the new plumbing in the hydrocarbon absorber oil loop. The absorber oil was metered into the system to produce a desired depth in the stripper column. At the end of run 80, the hydrocarbon stripper column had been pressurized from 1 atmosphere to 1270 kPa (184 psia).

At the beginning of run 81, the rich carbonate line was plugged with precipitated salts. The cold December weather was blamed for causing the bicarbonate to come out of solution. The lines were disassembled and washed out with water. Valves were placed between the carbon dioxide absorber and stripper so that steam could be vented from the stripper back through the 6-meter (20-foot) long rich carbonate line to preheat it prior to startup and to permit drainage of the line at the end of a run. Run 81 served primarily to complete the pressurization of the hydrocarbon stripper and to gain more familiarity with the better instrumented stripper column. Trouble was still encountered in obtaining good absorber oil regeneration as was evidenced by the olefin content of the by-product gas. The carbon dioxide reject stream was only about 98% pure which apparently reflected the lower gas flows used in the system and the resultant overscrubbing of the pyrolysis gases.

In purification run 82, lower flow rates of absorber oil were used to try to increase the hydrocarbon stripper temperature enough to properly regenerate the oil. Midway through the run, a leak was found at the new thermocouple located in the middle of the hydrocarbon stripper. The leak was repaired, but only after the stripper was depressurized. To increase the hydrocarbon stripper oven heat output, the oven thermostat was moved to the flue exhaust area and the oven thermocouple was relocated in the flue to monitor relative heat extraction. This alteration did not seem to greatly aid the temperature of the bottom of the stripper which stabilized at 232°C (450°F) and 2890 kPa (419 psia). However, the oil seemed to be regenerating better than usual as evidenced by the production of stripper off gas and the purity of the by-product gases (see Table 10). The exceptionally low C_2+ content (0.4%) of the by-product gas taken at 1430 hours is thought to have been influenced by the addition of fresh benzene a few minutes before the sample was taken. A new thermocouple located about one-third from the bottom of the hydrocarbon stripper showed that the temperatures were between 90 to 150°C (200 to 300°F) at that location in the column. The product gases which contained about 30% C_2+ were sent to the polymerizer. During the latter half of purification run 82, pyrolysis run 83 was made. This was the first time that the entire system was operated simultaneously, although admittedly at the different rates.

In view of the difficulty in attaining the desired temperature in the bottom of the hydrocarbon stripper, it was decided to lower the pressure of the stripper from 2965 to 2450 kPa (430 to 355 psia), and thus to raise the partial pressure of the absorber oil. A better stripping action was anticipated, since the boiling temperature of benzene at the lower pressure is 232°C (450°F). The hydrocarbon stripper started with a depth of 15 centimeters (6 inches) of absorber oil in it. However, early in run 83 there was a 33°C (60°F) temperature drop existing between the bottom of the hydrocarbon stripper and the thermocouple only about 56 centimeters (22 inches) higher. This drop seemed excessive and indicative of insufficient oil present. Absorber oil was added in increments equivalent to a depth of 5 centimeters (2 inches) in the stripper. This caused a gradual decrease in temperature part way up the column until an equivalent of 25 centimeters (60 inches) in height of oil had been added. The temperature of the thermocouple located one-third up from the bottom of the stripper then suddenly increased over 56°C (100°F). It appeared that inside the stripper, the absorber oil was not boiling as might be optimum, but rather that the cooler rich oil entering the column and the heat of vaporization of the desorbing gases were sufficient to prevent boiling temperatures from being reached. The rate of absorber oil circulation was reduced from 5.7 l/hr to 3.8 l/hr (1.5 to 1 gal/hr). The rate of the stripper product recovered did not appear to be reduced by this cutback in absorber oil flow and was about 60 l/hr (2 ft^3/hr). This amounts to only about 2% by weight of the rich oil that was recoverable gases and appears to say that poor regeneration of the absorber oil was a continuing problem. During the latter portion of the run, the bottom of the hydrocarbon absorber was raised from 121 to 146°C (250 to 295°F) to see if this would help to drive off the volatile by-product gases (hydrogen, carbon monoxide, and methane) before the rich oil left the absorber. The hydrocarbon stripper gas sample taken at 1400 hours reflects this increase in temperature by containing a significantly lower amount of the by-product gases. (The high propylene content seems to be a transient anomaly however.) This experiment indicated that the function of the hot portion of the hydrocarbon absorber needed improvement as well as that of the stripper. The gas collected in Booster 1 had one of the highest C_2+ contents obtained during the program (45.5% by volume or 52% by weight) as shown in Table 11. This product gas was fed to the polymerizer reactor.

TABLE 10. RUN 82 GAS ANALYSES (PERCENT BY VOLUME)

	Surge tank, 1120 psi	By-product gas, (1300 hr)	Hydrocarbon stripper gas, (1340 hr)	Booster 1, 1/8/79	By-product gas, 1/9/79 (1355 hr)	By-product gas, 350 psig (1430 hr)	By-product gas, 405 psig (1525 hr)	Booster 2, end of run
Hydrogen, H_2	9.13	20.06	5.90	6.64	19.21	19.49	18.81	5.36
H_2S	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Propane	0.04	0.03	0.09	0.03	0.04	. . .	0.03	0.11
Propylene	1.33	0.70	2.70	2.78	1.15	0.01	0.82	2.94
Isobutane	0.03	0.02	0.07	0.08	0.01	. . .	0.01	0.07
n-Butane	0.05	. . .	0.03	0.04	0	. . .	. . .	0.03
I-Butene	0.15	0.05	0.17	0.17	0.06	0.02	0.06	0.08
Isobutene	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Trans-Butene-2	0.40	0.05	0.52	0.63	0.13	0.03	0.07	0.56
cis-Butene	. . .	. . .	0.01	0.01	. . .	. . .	. . .	0.02
Isopentane	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
n-Pentane	0.02	. . .	. . .	. . .	. . .	. . .	. . .	. . .
CO_2	35.22	. . .	0.50	0.49	. . .	. . .	. . .	0.55
C_2H_4	6.87	2.03	20.66	21.18	0.56	0.02	0.12	23.15
C_2H_6	0.60	0.30	1.40	1.39	0.11	. . .	0.03	1.92
C_2H_2	0.59	0.13	1.58	1.77	0.06	. . .	. . .	1.62
O_2	0.22	0.19	0.17	0.19	0.07	0.19	0.22	0.15
N_2	4.44	8.78	3.84	3.57	6.17	9.16	8.89	6.07
CH_4	6.36	4.38	21.90	20.62	8.16	5.09	7.04	17.27
CO	34.18	63.19	40.08	39.59	64.01	65.65	63.61	39.23
$C_5^= + C_6 +$	0.35	0.10	0.36	0.81	0.25	0.33	0.29	0.87
$C_2 +$	10.43	3.4	27.59	28.89	2.37	0.41	1.43	31.37

TABLE 11. RUN 83 GAS ANALYSES (PERCENT BY VOLUME)

	Surge tank	By-product gas, end of run (1430 hr)	Booster 1 (1325 hr)	Hydrocarbon stripper gas (1400 hr)	Polymerizer off gas, end of run
Hydrogen, H_2	9.28	19.51	4.46	3.64	3.40
H_2S	0	0	0	0	0
Propane	0.05	0.01	0.11	0.44	1.44
Propylene	1.47	0.36	3.86	12.33*	7.33
Isobutane	0.04	0.01	0.06	0.12	0.04
n-Butane	0.05	0	0.02	0.05	0.49
I-Butene	0.16	0.04	0.03	0.26	0.59
Isobutene	0	0	0	0	0.14
Trans-Butene-2	0.45	0.06	0.41	0.60	0.18
cis-Butene	0.01	0	0.01	0.01	0.09
Isopentane	0	0	0	0	0.04
n-Pentane	0.03	0	0	0	0.09
CO_2	38.36	0.06	1.04	0.88	1.48
C_2H_4	7.18	1.52	34.70	36.45	21.84
C_2H_6	0.64	0.12	3.10	3.63	7.36
C_2H_2	0.82	0.06	2.97	3.96	0.08
O_2	0.07	0.09	0.04	0.04	0.09
N_2	2.38	5.14	3.02	1.49	3.02
CH_4	6.02	11.41	14.85	12.98	18.50
CO	32.47	61.29	31.06	22.78	33.34
$C_5^= + C_6 +$	0.52	0.31	0.24	0.34	0.47
$C_2 +$	14.52	2.49	45.51	58.19**	40.18

*Abnormally high (had just added some fresh benzene to absorber from reservoir).

**High due to propylene.

DISCUSSION

In this program, the hot-carbonate system for removal of carbon dioxide from pyrolysis gases was apparently shown to be very selective. It resulted in a very pure carbon dioxide stream. Because of minor contamination, however, it is doubtful that the low pressure carbon dioxide would have a market value. Optimizing the ratio of carbonate solution to raw pyrolysis gas could probably increase the carbon dioxide purity so that it could be released to the atmosphere without further purification to remove hydrocarbons, etc. The hot-carbonate system acted very much as was described by the literature. There may be naturally occurring water-soluble compounds in the raw pyrolysis gases which act to increase the absorption rates, because the system performed so well even with the short column lengths. It was observed that the carbon dioxide stream had a slight cinnamon oil odor, so there certainly were some oxygenated organics present in the system. Many oxygenated organic compounds apparently do increase the absorption rates, including sucrose, glycerol dextrose, ethylene glycol, levulose, methyl alcohol, ethyl alcohol, formaldehyde, and lactose.(48) Use of proprietary additives to the potassium carbonate solution (42)(49)(50) should be considered an option that probably will not be needed or that may be superfluous.

The hydrocarbon absorption and stripping systems need further tuning to achieve their potential. The best stripper product gases were attained when the pressure was reduced to about 2500 kPa (365 psia) which allowed the partial pressure of the benzene absorber oil to more closely approach the total pressure. A surprisingly large amount of heat into the stripper was needed to achieve regeneration of the absorber oil. The oil in the absorber was raised 100°C (185°F) with an apparent temperature difference of only 95°C (170°F) between the oven and the absorber bottom oil, whereas the stripper required a temperature difference of 250°C (450°F) to achieve a similar increase in temperature. It would appear that the latent heats of absorption (which serves to heat the absorber) and desorption (which cools the stripper) must be fairly high compared with the sensible heats involved. Further work with the bench-scale system could be done to decrease the amount of olefins lost in the by-product gases and to decrease the amount of by-product fuel gases in the stripper gas. Increasing the heat flux into the stripper by adding a heat-exchanger tube to circulate the oil by natural convection in the bottom section of the stripper would be helpful. Raising the rich oil inlet of the stripper would increase the effective length available for stripping, since no problems were encountered with excessive benzene in the stripper product gases. The hydrocarbon absorber appears to be not adequately vaporizing the by-product gases picked up by the absorber oil. The length of the absorber devoted to boiling off these gases should be increased, the incoming gases preheated, and possibly the temperature at the bottom raised.

Because the amount of pyrolysis gas stored in the surge tank is limited, steady-state conditions and compositions were not necessarily established by the end of each run, making mass balances very prone to error. It would be helpful to have used synthetic pyrolysis gas mixtures to check out the purification subsystems. If the program had been larger in scope, additional personnel could have been trained to run the somewhat troublesome pyrolysis system to keep the surge tank full and thereby to allow longer purification runs. However, at the end of the program the purification system was running very smoothly and all systems were operating simultaneously with only an engineer and a technician.

SECTION 6

POLYMERIZATION

BACKGROUND

In the early 1930s, the oil industry was faced with the need to obtain more gasoline per barrel of crude oil. It was found that the heavy oils (left after distilling off the straight-run gasoline) could be thermally decomposed (pyrolyzed) to produce a fairly high yield of gasoline. Unfortunately, about one-third of the products were of a gaseous nature and were composed primarily of unsaturated hydrocarbons; e.g., ethylene, propylene, and butylene. Efforts to convert these gaseous by-products to gasoline were fruitful and resulted in commercial application. Two major processes were commercialized for polymerizing the low-molecular-weight olefins: noncatalytic (thermal) and catalytic (usually phosphoric acid). The phosphoric acid process has the advantages of lower pressure and lower temperature, producing a gasoline having a motor octane value of 84 and a blending octane value (BOV) of 115, but it polymerizes ethylene with relative difficulty.(51)(52) The thermal process preferentially polymerizes ethylene,(53) and normally produces gasoline having a slightly lower motor octane value of 76 to 82 and a BOV of 85 to 100.(54)(40) However, it can be operated at higher temperatures to form a more aromatic gasoline with an octane rating of 100.(19) (These octane numbers are relative and are thought not to be equivalent to the octane values obtained by today's ASTM procedures.) The ability of the process to polymerize ethylene is quite important, since it was estimated that ethylene comprises 65 to 83% of the olefins formed by pyrolysis of cellulosics. Consequently thermal polymerization was chosen for the proposed process, but a small effort was contracted in the catalytic area.

Polymerization of olefins can proceed at atmospheric pressure and at temperatures on the order of 800°C (1500°F).(19) At these temperatures, the polymers formed are reactive and rapidly form naphthenic tars and char by the elimination of hydrogen. Polymerization under these conditions results in a product that is about one-half gasoline, which boils below 200°C and which consists primarily of benzene, and about one-half higher-boiling-point tar fraction containing large amounts of naphthenic hydrocarbons. It was recommended that hydrogen sulfide levels be kept below 1% to minimize the formation of rubbery by-products.(34) The length of time the gases spend in the polymerizing unit must be closely maintained to maximize the desired products.

Lower temperatures may be used to reduce tar formation; but higher pressures are needed to maintain the reaction rates. At 450°C (850°F) and 3450 kPa (500 psi), both ethylene and propylene polymerize to form liquids that are 80% gasoline with a C.F.R. Research octane rating of about 80. The ethylene polymerization rate is roughly twice that of propylene at these conditions. Increasing the pressure greatly increases the rate of polymerization, but with a slight decrease in the gasoline fraction and octane rating. For example, with ethylene, by increasing the pressure from 3450 to 20,685 kPa, the rate of liquid formation at 450°C is increased by a factor of about 10. However, the gasoline in the liquid product dropped from about 75% to about 65%, and the octane rating dropped from 78 to 63. The major advantage of the higher pressure is a large reduction in polymerizer unit size.(53) With a mixture of two parts ethylene to one part propylene, a single-pass conversion of 78% of the olefins to liquids was achieved at 4140 kPa and 400°C. These liquids were all in the gasoline to the JP-5 boiling range.(55)

The trash pyrolysis gases containing the highest reported hydrocarbon content were chosen to evaluate the feasibility of making polymer gasoline. On the basis that the C_2+ hydrocarbons were separated from the pyrolysis gases at high pressure and low temperature, preliminary calculations showed that more than sufficient energy was obtainable from combustion of the remaining gases to provide the heat of pyrolysis at a stack temperature of 980°C (1800°F). In addition, there was more than sufficient gaseous by-product fuel to use internal combustion engines for powering the shredder and compressing all the pyrolysis gases to 5170 kPa (750 psi). The polymer gasoline process has a relatively low process power requirement, and production will be constrained by the quantity of hydrocarbons in the pyrolysis gases. On this basis, at a 90% conversion of paraffins to olefins and of olefins to polymers,(55) the prediction for polymer gasoline production was 0.26 liter of gasoline and 0.09 liter of fuel oils per kilogram of dry organic material (or 62 and 21 gal/ton, respectively). This figure represented an energy conversion of 66% based on the low heating value (LHV) and used the results from pyrolysis of plastic-rich organics obtained from trash.(11) (This energy conversion figure has been revised to slightly over 50% based on NWC experimental results with a more cellulosic feedstock.)

In pyrolysis gases formed at 935°C, C_2+ saturated hydrocarbons are ethane at 2.2% and butane at 13.6% by weight of the hydrocarbon fraction.(7) Nonpolymerizable compounds having low molecular weight, such as hydrogen, methane, ethane, propane, and butane, will be formed as by-products of the dominating polymerization reaction. These gases will tend to be concentrated in the noncondensable, gaseous product stream leaving the polymerizer. These gases may be recycled through the low-pressure pyrolysis reactor to reform the saturated hydrocarbons to ethylene, propylene, etc. The pyrolysis of ethane can result in an 89% by weight yield of ethylene per pass based on the ethane consumed at 825°C with short residence times. Side reactions during the cracking of ethane produce methane (6%), propylene (3%), and acetylene (1/2%).(56) The yield of olefins from the pyrolysis of butane at 1 atmosphere and 700°C is also about 90% by weight, although the olefins yield from butane is considerably less at higher temperatures.(55)

ETHYLENE

Experimentation

To gain insights into the exothermic polymerization reaction, an experimental reactor was constructed as shown in Figure 33. This polymerization effort was conducted concurrently with the pyrolysis development, so no purified pyrolysis gases at elevated pressures were available for use. Since ethylene was the largest single constituent in the gasoline precursors found in the pyrolysis gases, bottled ethylene was purchased and used for this study. Technical grade ethylene flows from the storage bottle through a remotely operated valve into a coil fabricated from 304 stainless steel tubing. Two coils were fabricated--one from 0.95-centimeter (3/8-inch) outside diameter tubing having a volume of about 80 cc and the other from 1.27-centimeter (1/2-inch) outside diameter tubing with a volume of 260 cc. The coil is immersed in a fluidized sand bath which provides a heat-transfer medium for temperatures up to 600°C. A water-cooled condenser cools the gasoline before it enters the receiver. The gases are regulated down to near atmospheric pressure where the flow rate is monitored and controlled by a rotameter. The unpolymerized gases are then flared off.

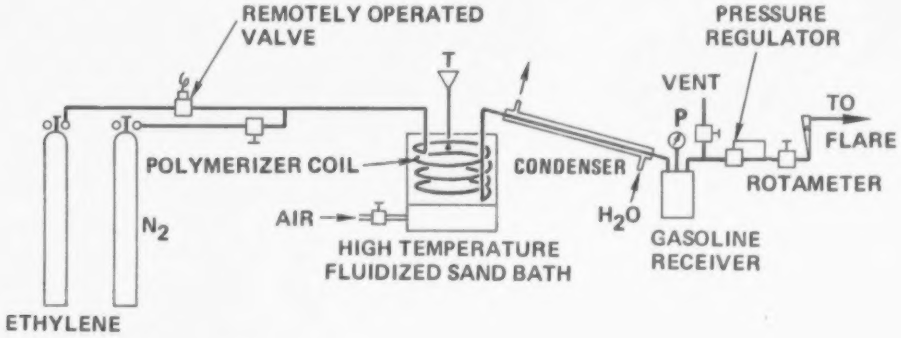


Figure 33. Laboratory Scale Polymerization Flow Sheet.

A series of 25 tests was run using the laboratory apparatus described previously. It is important to note one significant difference in operation of the laboratory unit and a scaled-up system. In the laboratory system the flow rate of gases exiting from the system is controlled, while in the larger unit the flow of gases entering the system would be controlled. Thus, in the laboratory unit, for any given experimental run, the quantity of ethylene entering the polymerizer is determined after the test by summing up the quantities of liquid and gaseous products measured during and after the test.

In general, the tests were conducted as follows: After the sand bath had reached operating temperature, the system was purged with nitrogen at low pressure. The timing of each run started with the opening of the remotely operated valve which pressurized the system with ethylene to an operating pressure controlled by the ethylene pressure regulator. The flow rate on the rotameter was then set. Data taken during the run at 5-minute intervals were: sand bath temperature, pressure on the gas receiver (same as on the coil), and flow rate of exit gases. At the end of a test, closing of the remote valve signified the end of the timing interval. The pressure in the system was bled off downstream of the gasoline receiver. This procedure purged the condenser of any gasoline present. The gasoline collected was then weighed and the volume measured. A small sample of each run was filtered to remove fine carbon particles so that the color of the sample was evident. The samples ranged in color from light straw color to a dark orange. The more severe conditions--higher bath temperatures and higher pressures--yielded darker product which was of a higher molecular weight.

The data for the successful runs are presented in Table 12. In some of the runs, the flow rate out of the system was zero. This was not generally planned but occurred naturally as a result of the downstream regulator becoming plugged with fine carbon particles. This problem was solved by placing a 10 μm filter in the line upstream of the regulator. However, it is interesting to note that even with a closed system, gasoline was produced at fairly respectable rates. While all of the tests yielded at least a trace of carbon in the gasoline product, on occasion with a combination of temperatures above 498°C (900°F) and at pressures greater than 3448 kPa (500 psi) large amounts of carbon were formed. The larger coil plugged up on run 14 where the pressure was 6895 kPa (1000 psi) and temperature was 524°C (975°F). The plugging occurred at a section about 5.08 centimeters (2 inches) long located about 30.48 centimeters (12 inches) from the inlet to the coil. (This fact will become more significant later when an analytical model of the polymerizer coil is discussed.)

Test runs 20 through 23 were made for the purpose of obtaining a sufficient amount of gasoline for octane tests. The liquid product from these tests was distilled following ASTM distillation procedure D-86. A distillation curve for the liquid product is shown in Figure 34. Ninety percent of the liquid boiled below 200°C. However, for the octane tests, the gasoline fraction was taken at 180°C and comprised 85% of the liquid product. The octane number of the gasoline fraction was found to be 90 using the ASTM motor method. (The motor method typically yields lower octane numbers than the research method.) Regular gasoline sold as having an octane of 88 tested out at 87. Blends of 25% and 50% by volume polymer gasoline in this same regular (leaded) gasoline did not change the octane rating of the regular gasoline.

A heating value test was also run on the polymer gasoline sample using a Parr oxygen bomb calorimeter. A higher heating value of 44.2 kJ/g was obtained. In comparison, the higher heating value of "isooctane" is 47.8 kJ/g, while that of ethylbenzene is 43.0 kJ/g. The high octane rating along with the intermediate heating value suggests that the gasoline consists chiefly of unsaturated liquids.

Further tests were run using a 15-kilowatt (20-horsepower) rotary Wankel engine. The Wankel engine was designed to operate on a mixture of gasoline and oil (50:1 mixture ratio). No difference in starting or operation of the engine was detected whether using the crude polymer gasoline, the distilled polymer gasoline fraction, or the gasoline/oil mixture.

TABLE 12. POLYMERIZATION TEST DATA SUMMARY

Run no.	Coil volume, cm^3	Bath temperature, °C	Coil pressure, kPa (psia)	Run time, min	Ethylene input, g/min	Gas out, std cc/min	Residence time, min	Gasoline production, cc/hr	% conv. to gasoline	% conv. Eq. pg. 82	Remarks
3	80	454	6998 (1015)	135	?	0	?	14.2	?		
4	80	449	7343 (1065)	120	?	0	?	41.0	?		Plugged
5	80	468	5275 (765)	120	0.30	0	8.0	25.8	?		
6	80	488	3551 (515)	270	0.02	0	75.6	1.8	?		
7	80	385	4137 (600)	90	. .	600/1,200	?	0	0		
8	260	477	5619 (815)	90	1.16	600	4.5	38.5	42.0	46.4	
10	260	427	3551 (515)	45	0.80	600	5.7	8.0	11.7	15.8	
11	260	432	5275 (765)	90	1.22	600	5.3	43.3	42.7	23.3	
12	80	413	5413 (785)	65	0.89	600	3.0	15.7	20.2	7.5	
13	260	407	5413 (785)	120	0.38	0	17.7	32.5	?		
14	260	524	7136 (1035)	45	0.91	600	8.4	17.3	21.1	85.5	Plugged, leak
15	260	454	7205 (1045)	45	?	600/300	?	72.0	?		
16	260	446	6688 (970)	45	0.83	150	9.4	56.0	79.0	51.8	
17	260	449	6171 (895)	30	1.04	500	7.7	38.0	44.0	44.6	
18	260	468	6998 (1015)	45	?	150/600	?	89.0	?		
19	260	438	6998 (1015)	90	0.91	460	9.5	31.3	39.7	43.8	Leak
20	260	449	5170 (750)	180	1.39	600	4.6	56.7	50.0		For octane tests
21	260	452	5170 (750)	180	1.50	600	4.2	65.8	53.4		
22	260	432	5170 (750)	210	1.16	600	5.5	38.0	39.5		
23	260	454	5170 (750)	285	1.51	600	4.1	68.4	54.0		
24	260	443	5100 (740)	120	3.30	2050	1.8	78.5	28.0		
25	260	443	5200 (755)	155	3.27	2050	1.9	75.9	27.2		

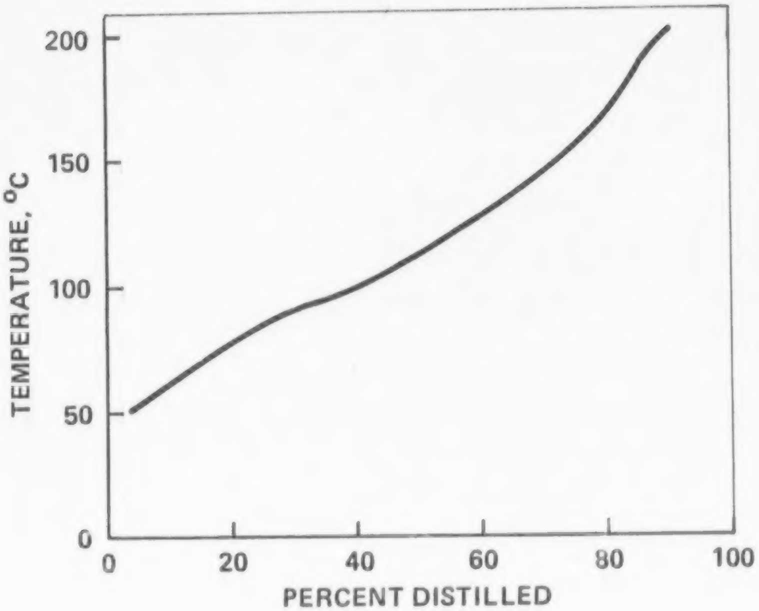


Figure 34. Distillation Curve for Polymerized Ethylene.

Samples of polymer gasoline have been stored in the office area for over 3 1/2 years with no visual evidence of gum formation or other long-term storage problems. Apparently the polymer gasoline formed by the noncatalytic, thermal method results in a stable material that does not polymerize further during long-term storage at room temperature. The use of antioxidants or inhibitors to prevent gum formation will probably not be necessary with this gasoline product.

The results described above indicate that the polymer gasoline produced from ethylene gas (a major constituent of pyrolysis gases) can be used as an automotive fuel after filtering and distillation.

Discussion

In an attempt to interpret the data and compare it with published data,(53) estimates of the residence time in the coil were calculated from the known volume of the coil and the volume flow rate of the ethylene at the operating conditions. This correlation with similar conditions in the literature did not often work, and at times it appeared that the smaller coil was just as efficient as the larger coil for producing gasoline. It was felt that the production of carbon plugs was due to hot spots in the coil.

The key variables in the polymerizer operation are temperature, pressure, residence time, and mole fraction of olefins in the feed. Reaction rate data and an algebraic expression relating the fraction of olefins reacting in a given time to the above-mentioned variables were found in the literature.(54)

These rate data were used to obtain an Arrhenius expression for the reaction rate constant. These equations are given as follows:

$$x = \frac{(K_2/p)atp}{1 + (K_2/p)atp}$$

where the Arrhenius expression for the reaction velocity constant divided by pressure, K_2/p, is given by:

$$K_2 2/p = 2763\ e^{-(13,656/T)}$$

where

x = the fraction of olefins converted in time t

a = the mole fraction of olefins in the feed

t = time, minutes

p = pressure, kPa

T = temperature, °K

The influence of the operating variables on conversion of olefins as predicted by the above equations is presented in Figures 35 and 36.

While this equation afforded insight into the relationship between variables, the agreement with the data was poor in most cases. In Table 12, the conversion predicted by the above expression for selected runs at the bath temperature is listed along with the observed percent conversion. First of all it must be realized that the calculated conversion is of ethylene to liquid plus gases, while the measured conversion is only to gasoline, since the outlet gases were not analyzed. From run 12, for example, since the measured conversion was significantly higher than the predicted conversion, the conclusion must be drawn that the actual temperature within the coil must be much higher than the sand bath temperature (which is very close to the coil wall temperature). In fact, from the expression given above, the temperature would have to be around 454°C (850°F) or about 56°C (100°F) hotter than the tube wall to yield the observed conversion. Similar qualitative conclusions can be drawn from the comparisons for runs 11 and 16.

In run 10, on the contrary, the conditions are sufficiently mild that the gas temperature should be closer to the bath temperature. Hence, the predicted and observed values of conversion should be as close as they are.

By the same analysis, one would be led to suspect the data for runs 8, 17, and 19 since under these severe conditions the measured conversion values should be much higher than the predicted values.

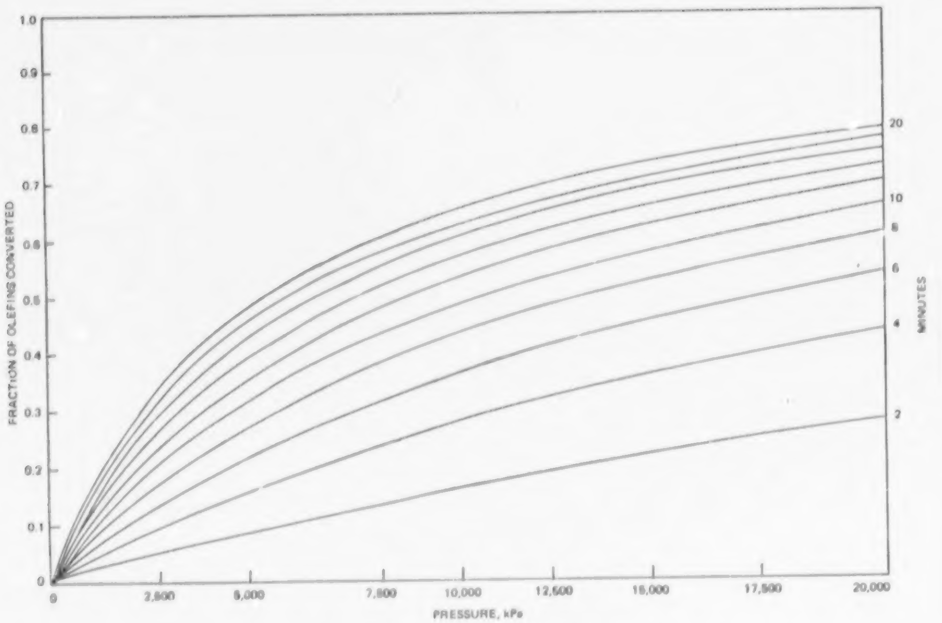


Figure 35. Predicted Extent of Conversion of Olefins at 427°C (800°F).

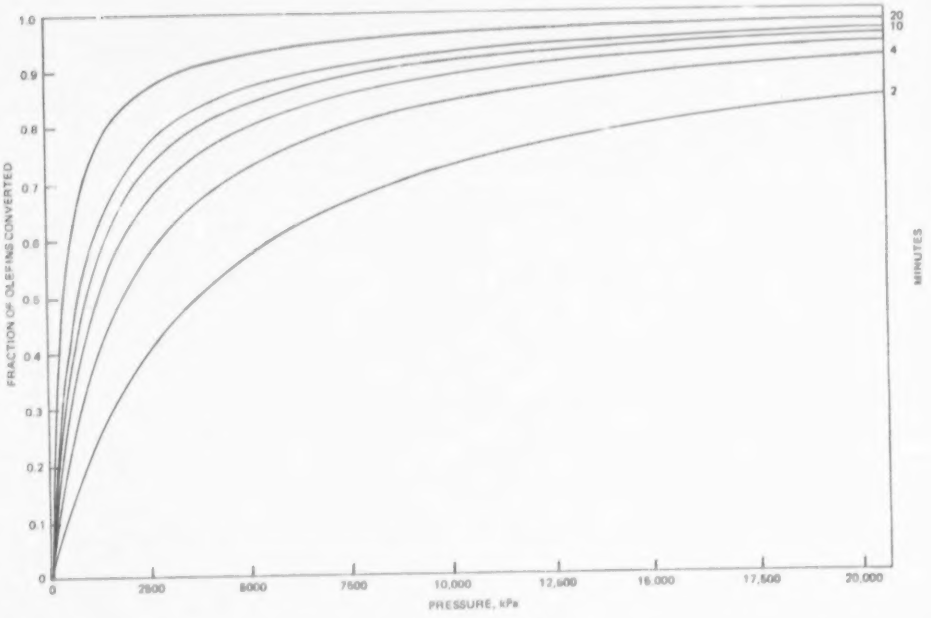


Figure 36. Predicted Extent of Conversion of Olefins at 538°C (1000°F).

Since the rate expression appeared to afford agreement with some of the data, particularly where the measured temperature was close to the gas temperature, a more ambitious analysis was undertaken. Basically, this analysis treats a mixture of ethylene, gasoline, and one other gaseous specie flowing along a tube immersed in a constant-temperature bath. For the sake of argument, the polymerization reaction was postulated to be as follows:

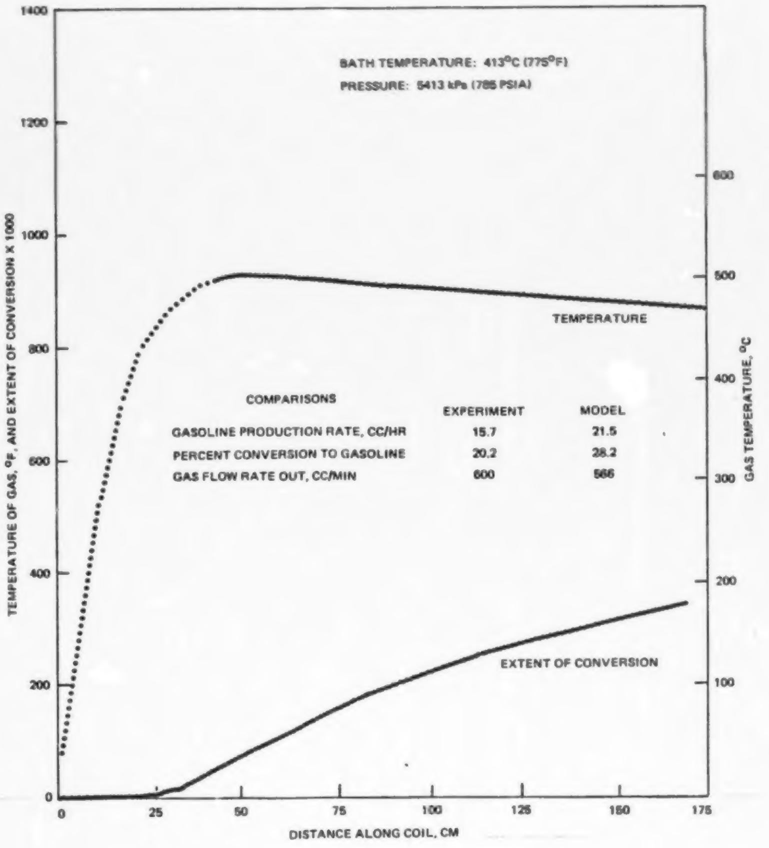
$$5C_2H_4 \longrightarrow C_8H_{18} + C_2H_2 \qquad \Delta H = -92.9\ \mathrm{kJ/gmole}\ (-40{,}000\ \mathrm{Btu/lb\text{-}mole\ ethylene})$$

While gas sampling has shown that the main gas species after polymerization of ethylene are ethane and methane, the mixture of the two gases has about the same molecular weight as acetylene. Octane was taken as the product having about the right molecular weight for the liquid product. The heat of polymerization chosen is that value recommended for design purposes.(54) The tubular reactor as described above was analyzed using a finite-difference scheme for solving the resulting first-order differential equation expressing the energy balance on the system.

The resulting model was used to attempt to understand what was happening within the coil under various operating conditions. It appears that the model does reveal some important aspects of the polymerization reactor and can be used profitably as a design tool. A few examples should suffice to demonstrate this point. Figure 37 presents the predicted temperature and percent conversion of ethylene vs. distance along the reactor for the conditions of run 12. Under these operating conditions, it is apparent that had the coil been longer a greater conversion could have been achieved. Shown on the figure is a comparison between predicted and observed values. While the agreement is far from perfect, considering the crudity of the model, the results appear promising. The model was tested further by analyzing run 14, which plugged up with carbon as mentioned earlier. The temperature and percent conversion curves are presented in Figure 38 for this case. The temperature spike predicted by the model is suggestive of carbon deposition occurring at that location.

The analysis for run 16 presented in Figure 39 suggests that a much shorter coil can be used if the operating conditions are carefully controlled. In this run, only a small amount of carbon was observed, indicating that the temperature spike was not too great in this case. The predicted and measured values are quite close for this run.

The final examples involve the design of the scaled-up polymerizer. The original intent was to accommodate the 16-fold increase in flow rate by increasing the length of the coil, but keeping the tubing diameter small (on the order of 1.905 centimeters (3/4 inch)) so as to increase the Reynolds number and, hence, the heat-transfer coefficient. The prediction for this set of conditions is shown in Figure 40. A runaway reaction was predicted to occur after the heating of the ethylene to the bath temperature when the exothermic heat release overpowered the ability of the reactor tube walls to transfer the heat away. Clearly, under these conditions, the coil would surely coke up. This example suggests that the scaled-up polymerizer should consist of multiple tubes--each one operating close to the operating conditions of the laboratory scale unit. This



COMPARISONS	EXPERIMENT	MODEL
GASOLINE PRODUCTION RATE, CC/HR	15.7	21.5
PERCENT CONVERSION TO GASOLINE	20.2	28.2
GAS FLOW RATE OUT, CC/MIN	600	566

Figure 37. Predicted Temperature and Conversion for Run 12.

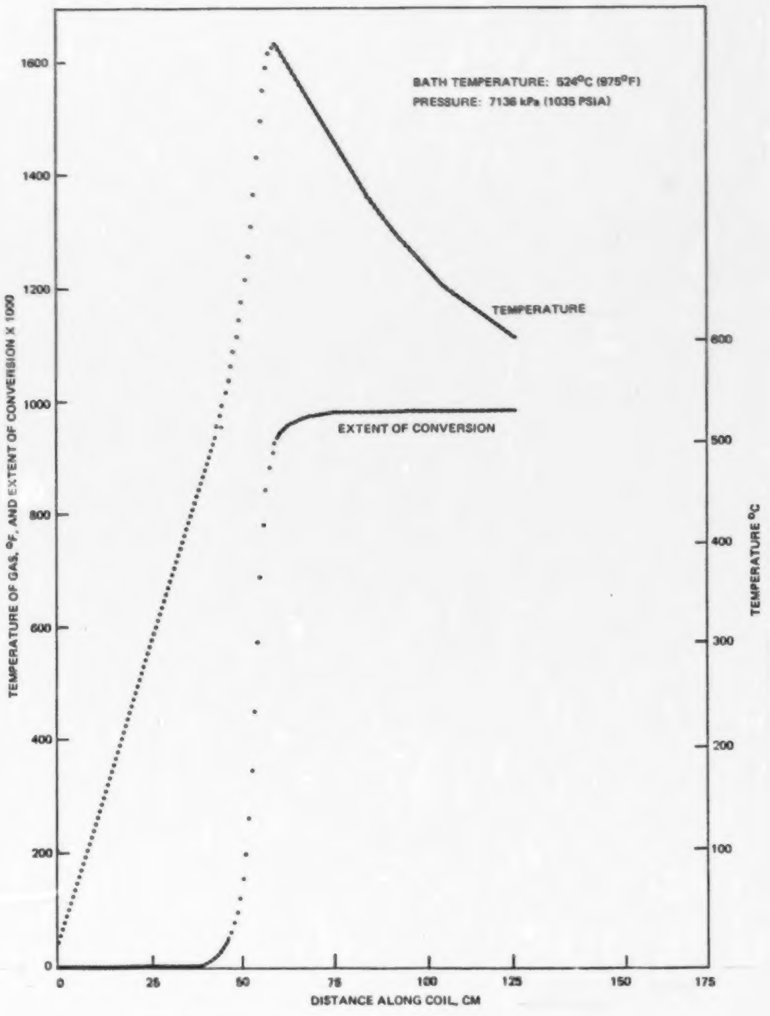
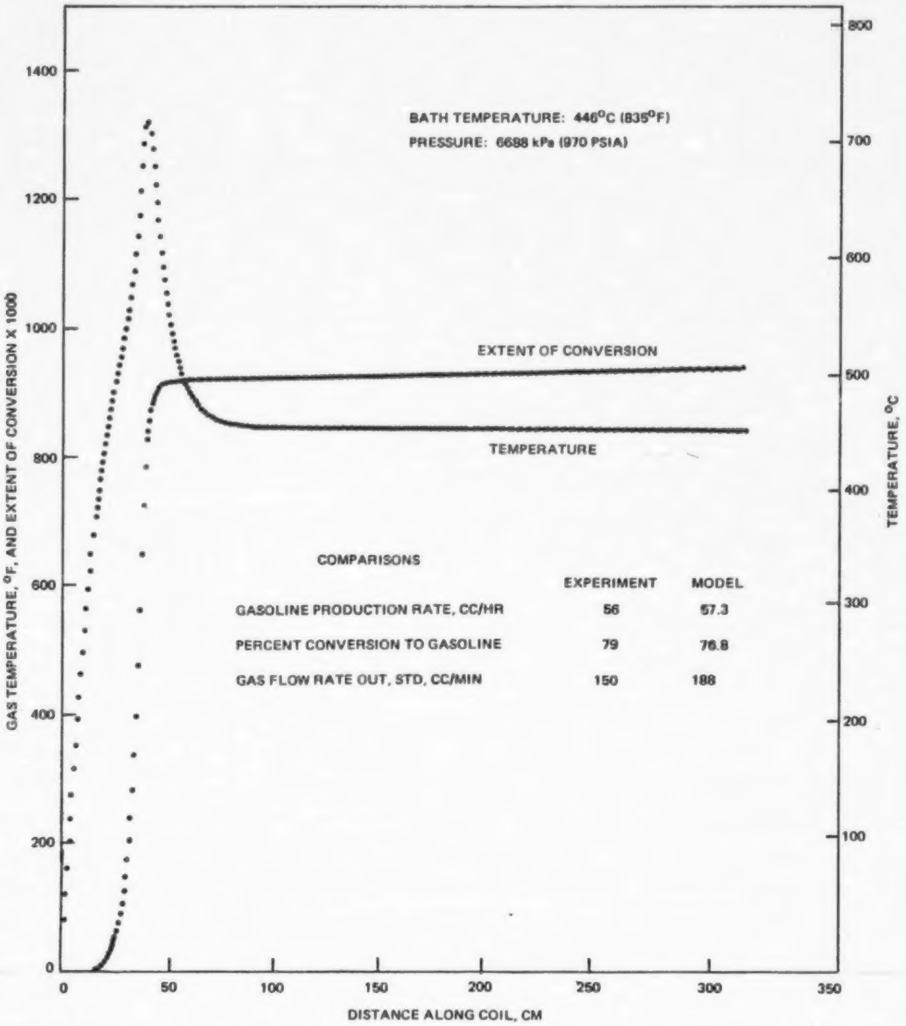


Figure 38. Predicted Temperature and Conversion for Run 14.

design would then be comprised of 16 parallel 1.27-centimeter (1/2-inch) tubes about 1.83 meters (6 feet) long.



COMPARISONS

	EXPERIMENT	MODEL
GASOLINE PRODUCTION RATE, CC/HR	56	57.3
PERCENT CONVERSION TO GASOLINE	79	76.8
GAS FLOW RATE OUT, STD, CC/MIN	150	188

Figure 39. Predicted Temperature and Conversion for Run 16.

The last two polymerization tests (tests 24 and 25) were run for further checkout of the mathematical model of the polymerization reactor. From comparisons between theory and experiment, it appears that the polymerization reaction can be expressed as follows:

$$C_2H_4 \rightarrow 0.2L_{125} + 0.1G_{30} + \Delta H$$

$\Delta H = -92.9$ kJ/mol (-40,000 Btu/lb-mole) for each union of two olefin molecules

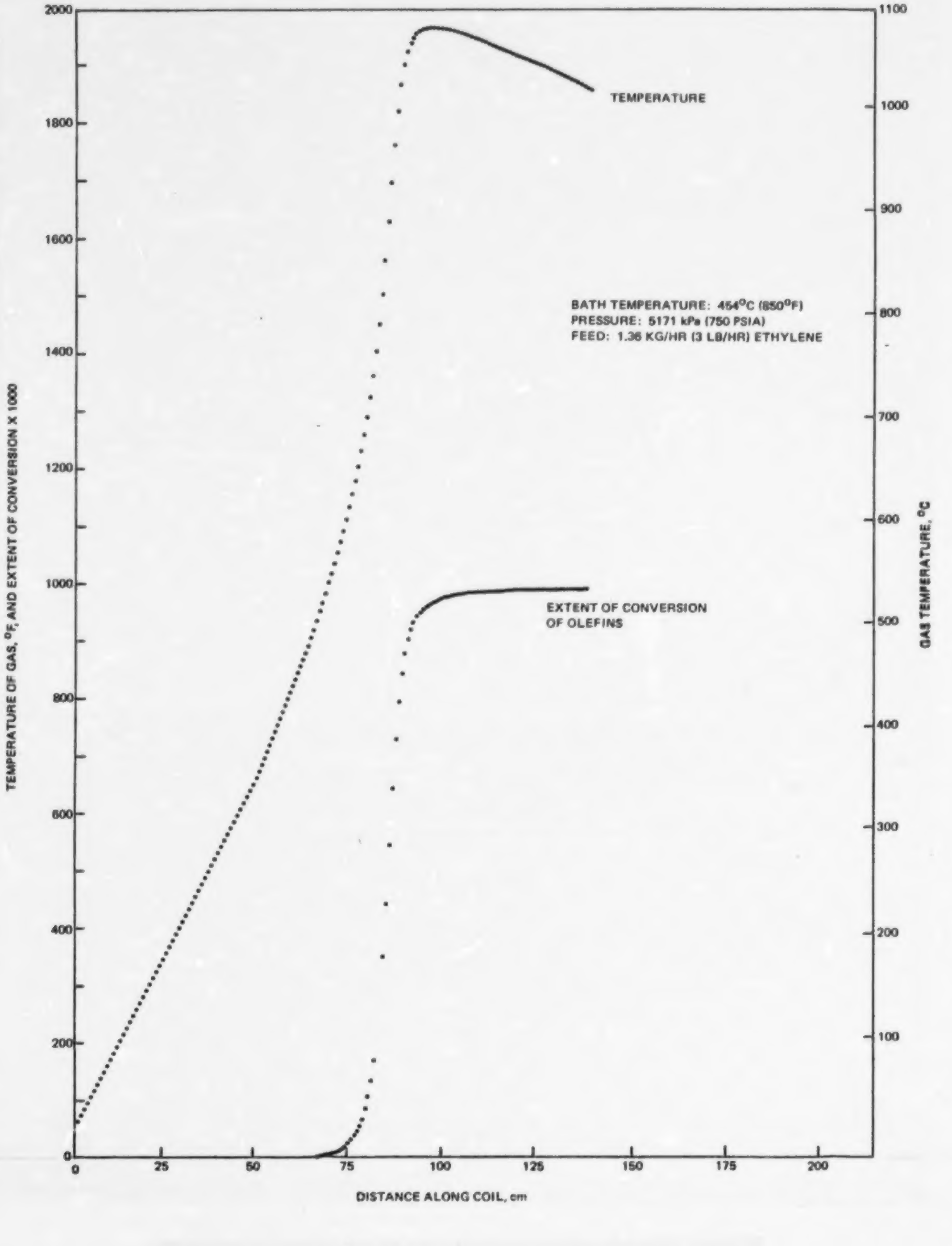


Figure 40. Predicted Temperature and Conversion for Scaled-up (Longer) Polymerizer.

This expression indicates that for each mole of ethylene polymerized, 0.2 mole of liquid having a molecular weight of about 125 and 0.1 mole of gases having an average molecular weight of 30 are produced. It follows, therefore, that about 90% by weight of the ethylene is converted to a liquid product.

Gas samples taken of the effluent from the polymerization coil indicate that the by-product gases produced in the reaction are primarily methane and ethane. Eventual conversion of 90% of the ethane to gasoline may be accomplished by passing the noncondensable gas from the polymerizer through the pyrolysis coil to crack the ethane to ethylene.(19)

To determine the effects of operating the polymerizer with the olefin scrubber and stripper in a recycle loop, an analysis was performed using the previously developed mathematical model of the polymerizer. A simplified diagram of the system is analyzed in Figure 41.

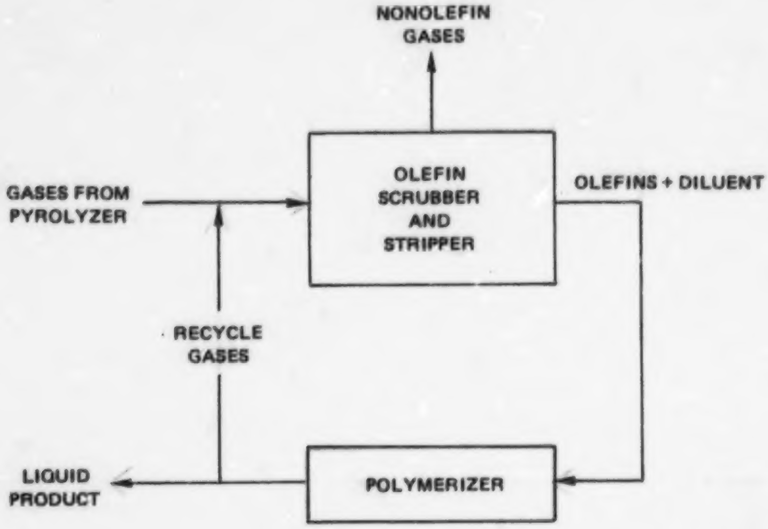


Figure 41. Polymerizer Recycle Loop.

For a given gas flow rate and composition from the pyrolysis unit, tradeoffs exist involving the amount of conversion per pass through the polymerizer and the attendant losses in the absorber and stripper with recycle. In other words, the longer the polymerizer tubes, the greater the conversion of olefin to gasoline per pass; hence, less recycle is required.

The results are presented in Figure 42 for a system capable of handling the output of the 4.54 kg/hr (10 lb/hr) pyrolysis system (1.1 kg/hr (2.4 lb/hr) of olefins). The analysis was also based on the assumption that 95% of the olefins would be recovered from the absorber/stripper unit and the gases entering the polymerizer would be diluted with 10% of inert gases. From

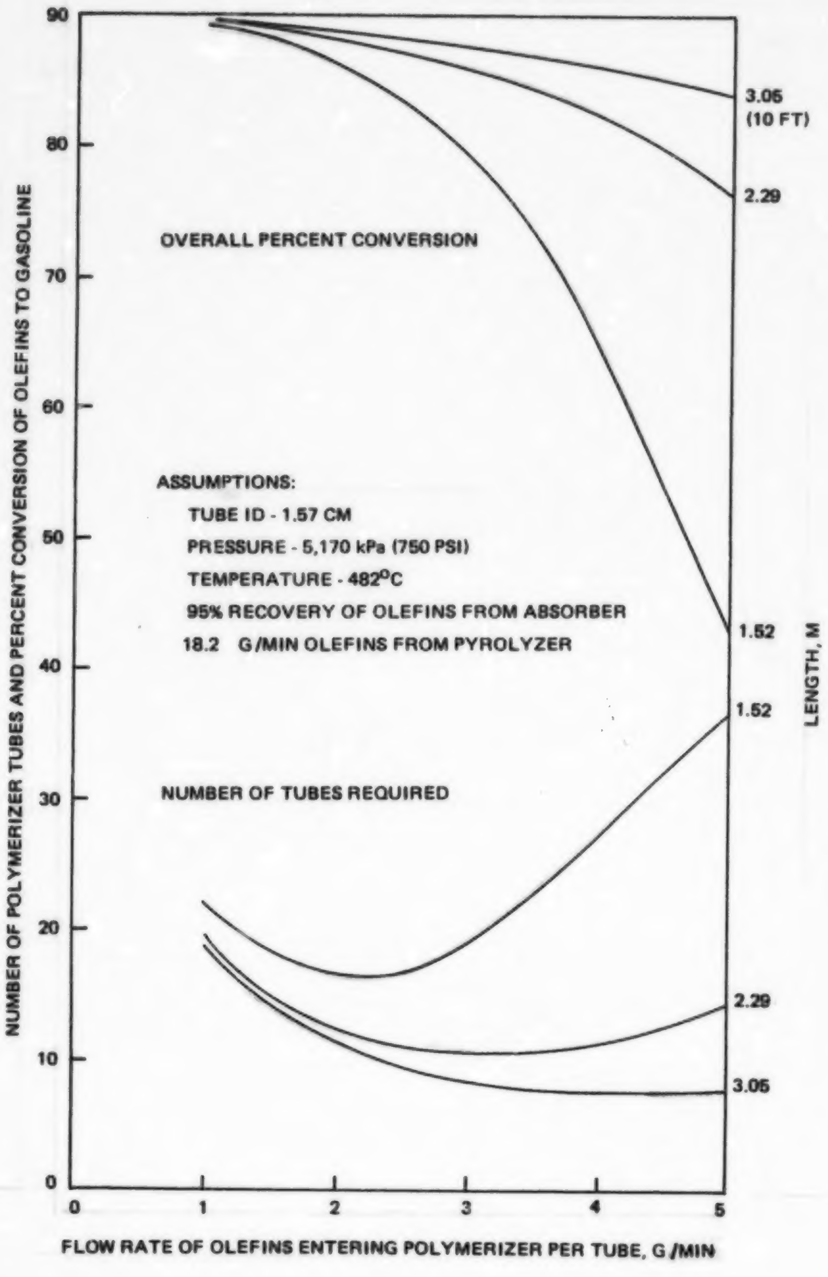


Figure 42. Effect of Olefin Flow Rate on Conversion Efficiency and Number of Tubes Required.

Figure 42, it can be seen that with a flow rate of 2.5 g/min of olefins per tube entering the polymerizer, about 10 tubes (3 meters long) would be required and that 88% of the olefins would be converted to gasoline.

While the design of a polymerizer to handle the output of the existing pyrolysis unit (4.54 kg/hr) has been established, the scaled-up unit was not fabricated because the cost and time factors appeared to be too large for the present program. This design was also based on 90% olefins in the feedstock, whereas the purification system was still being debugged and was producing feedstock with less than 50% olefins. The lower olefin content of the polymerizer feedstock would greatly reduce the heat transfer problem and necessitate the addition of a long-residence-time soaking chamber to obtain the desired high conversion per pass.

PURIFIED PYROLYSIS GASES

Experimentation

From the experimentation with ethylene, it was apparent that temperature control of the polymerizer was critical. As the ambient temperature olefins enter the reactor, they are first heated until the polymerization reaction rate is sufficiently high that the constant-temperature bath will remove the exothermic heat of reaction. The mathematical model suggests that the system will be optimized with very high transfer rates through the reactor wall to the cooling medium. A fluidized sand bath was used satisfactorily as the cooling medium for the laboratory experiments with pure ethylene, but a simpler approach was desired. The simplest system was thought to be one which boiled a liquid at the desired temperature. Any hot spots in the reactor would boil the liquid at that location, giving rise to the very high heat-transfer rates associated with boiling. If the cool entrance section of the reactor were placed above the boiling constant-temperature bath, the very high heat-transfer rates associated with condensation would be attained. Unfortunately, the organic liquids normally used for heat transfer at elevated temperatures decompose at the temperatures useful for polymerization. Among the inorganic materials potentially useful, a brief search revealed that at 101 kPa (14.7 psia), mercury boils at 357°C (675°F) and sulfur at 445°C (833°F). The cost and toxicity of mercury precluded its further consideration.

Sulfur melts at 112°C and becomes less viscous as the temperature is raised. However, after only a small increase in temperature, the viscosity increases with temperature and reaches a maximum at about 187°C, at which temperature the sulfur is too viscous to flow. The increase in viscosity is apparently due to the polymerization of liquid sulfur to S_8. As the temperature is further increased, the viscosity slowly decreases so that at the boiling point, sulfur has very good properties. Although small quantities of iodine added to sulfur were reported to be very beneficial in reducing the sulfur viscosity at temperatures near the melting point so that sulfur could be used for heat pipe applications,(57) it was decided not to use this refinement since the viscosity at the operating temperature is quite low. Elemental sulfur is apparently not very corrosive to 316 stainless steel with corrosion rates of 0.5 mm/year at 454°C being reported.(58)

A polymerization reactor was constructed as shown in Figure 43. The reactor itself was made of a 305-centimeter (10-foot) length of 1.25-centimeter (1/2-inch) 316 stainless steel tubing bent into a trombone-slide shape. The inlet and outlet were both at the top of the reactor and passed through the bulkhead of the sulfur bath container. The boiling sulfur bath was a salvaged stainless steel container 9.5 centimeters inside diameter by 70 centimeters long with a single flanged opening at the top. (This container was the original pyrolysis reactor used temporarily in the early phase of the program.)

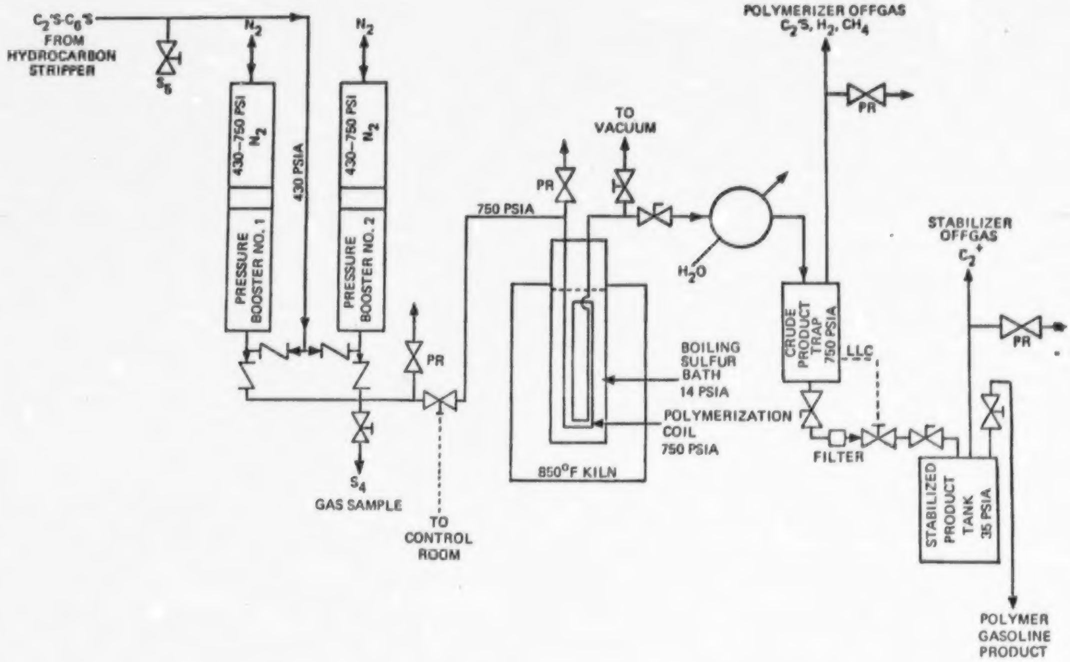

C_2'S-C_6'S FROM HYDROCARBON STRIPPER
S_5
N_2
N_2
430–750 PSI N_2
430–750 PSI N_2
430 PSIA
PRESSURE BOOSTER NO. 1
PRESSURE BOOSTER NO. 2
PR
S_4
GAS SAMPLE
TO CONTROL ROOM
750 PSIA
PR
TO VACUUM
H_2O
BOILING SULFUR BATH
14 PSIA
POLYMERIZATION COIL
750 PSIA
850°F KILN
POLYMERIZER OFFGAS
C_2'S, H_2, CH_4
PR
CRUDE PRODUCT TRAP 750 PSIA
LLC
FILTER
STABILIZER OFFGAS
C_2^+
PR
STABILIZED PRODUCT TANK 35 PSIA
POLYMER GASOLINE PRODUCT

Figure 43. Bench-Scale Polymerization Reactor.

The boiling sulfur bath was placed inside of an electric tubular furnace so that the top 15 centimeters of the bath was air cooled. The sulfur level was adjusted to be about the same as the top of the electric furnace. The polymerizing reactor temperature was measured by a sheathed thermocouple inserted about 50 centimeters into the reactor inlet. The temperature of the sulfur bath was monitored by a 0.64-centimeter (1/4-inch) sheathed 316 stainless steel thermocouple immersed in the sulfur. A temperature controller-recorder maintained the desired temperature as long as it was set below the boiling temperature of the sulfur. The boiling temperature of the sulfur was adjusted by changing the total pressure above the sulfur. Quite good agreement was found with the sulfur vapor pressure data in the literature.(18) After 60 hours of continuous operation at 454°C, the brass bourdon tube of the pressure gauge was corroded through. The escaping sulfur gases ignited, but caused very little damage. Upon disassembly, it was found that the copper gasket used in the flanged fitting was also badly corroded. The gasket was changed to 304 stainless steel. It was decided that the pressure could be estimated more accurately from the temperature measurement than from a pressure gauge, so the use of a pressure gauge on the sulfur bath was discontinued. The boiling sulfur bath thereafter proved to be a trouble-free constant-temperature bath.

During the concern over corrosion by the boiling sulfur, samples of aluminum-coated stainless steel (Alonized^{TM}) were obtained, measured, and placed in the sulfur bath. After approximately 1 year of intermittent operation during the program, the Alonized samples had not been measurably corroded, although their appearance was much darker in color. In contrast, the stainless steel surfaces had a very thin black coating on them which could be peeled off. No irregular corrosion or pitting was noted on the stainless steel surfaces immersed in the sulfur bath.

The polymerization portion of the program was relatively limited due to the problems encountered with the purification system. The first polymer gasoline was made from the impure gases available from run 58 which had only a 16% olefin content. The sulfur bath and the polymerizer temperatures were virtually identical at 454°C (850°F) which reflects the relatively slow reaction rates and heat release at these low partial pressures. The total pressure was 5170 kPa (750 psig). Only a few drops of condensate were recovered when the polymerizer was vented at the end of the run.

Using "purified" pyrolysis gases from the purification experiment (run 59), which demonstrated the undesirable absorption of carbon dioxide in the absorber oil, a small quantity of gasoline was produced in the polymerizer. These gases which were fed to the polymerizer contained about 48% carbon dioxide, 7% carbon monoxide, 0.6% hydrogen, 10% nitrogen, 7% methane, and the remainder (only 27.4%) C_2+ hydrocarbons. The polymerizer at 474°C (885°F) and 5270 kPa (750 psig) acted as expected to slowly polymerize the ethylene and propylene to form gasoline. There were no apparent catalytic impurities derived from the MSW feedstock to cause the polymerization to behave abnormally. Infrared absorption techniques verified that the gasoline product was of a hydrocarbon nature with an absence of indications of oxygen. The product had an amber color with a gasoline appearance and odor.

After the hot carbonate system was installed, with purified pyrolysis gases from run 75 containing nearly 48% C_2+ hydrocarbons, an additional small quantity of gasoline crude was produced. However, the average percent of olefins fed to the polymerizer was only about 31% by volume. The reactor was operated at 5270 kPa (750 psig) and 477°C (890°F). Based on a nitrogen mass balance, about 65% of the ethylene entering the polymerizer reacted to form polymer gasoline. This yield is lower than desired due to the relative impurity of the feedstock gases. The polymerizer appeared to be acting qualitatively as expected based on the experience gained with pure ethylene.

The polymerizer reactor was also fed hydrocarbon stripper product gases from runs 78, 82, and 83. The olefin content varied from 35 to 46% by volume. The polymerizer temperature was 480°C (895°F). The flow rate of polymerizer off gases was about 1.5 that used in previous runs or about 600 cc/min (1.2 ft^3/hr). At the end of these three runs, 112 cc of polymer gasoline crude was recovered. This synthetic crude was distilled using ASTM D-86 procedure, with the result that 93% of the crude was distilled in the gasoline boiling range. The gasoline fraction had a density of 0.755 g/cc, whereas the residual oil fraction had a density of 0.915 g/cc. The residual oil had a low apparent viscosity. The distillation curve is shown in Figure 44 for both the ECO II and the pure ethylene-derived synthetic crude oil products for comparison. These curves match each other very closely as well as the ASTM D-430 gasoline designated "B". Not enough polymer gasoline was made from pyrolysis gases to run octane tests.

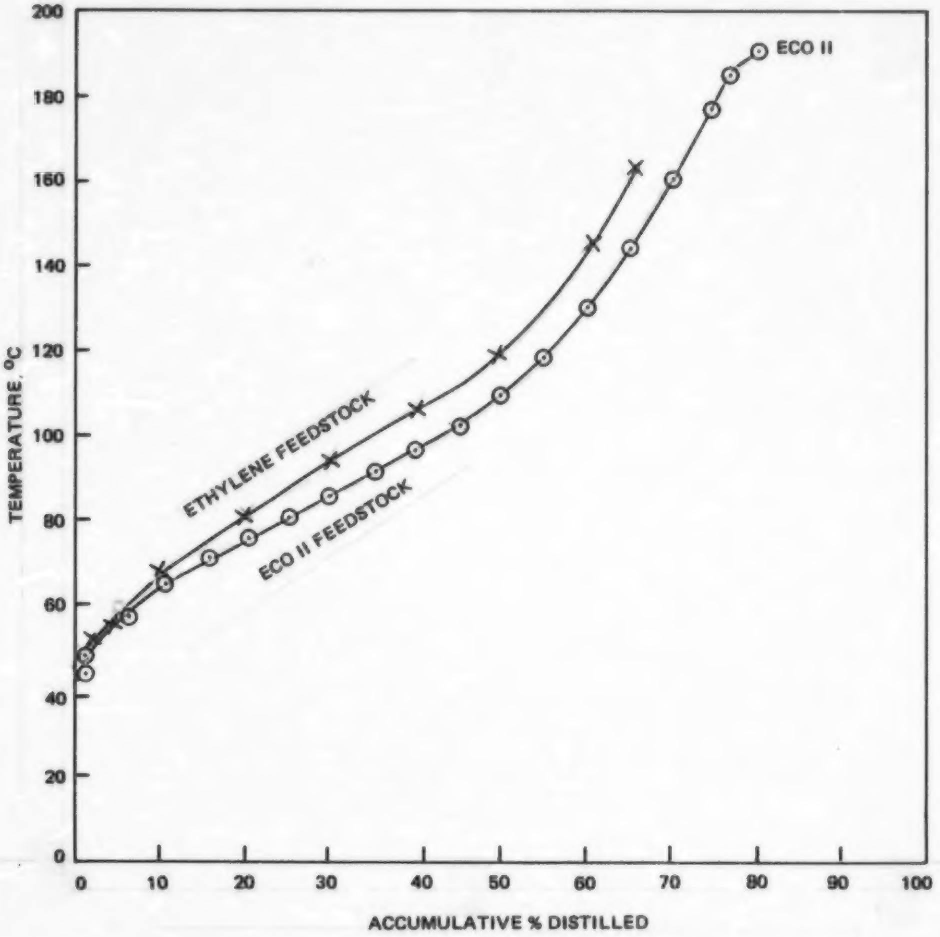


Figure 44. Distillation Curve for Synthetic Crude Oil Derived from ECO II and Ethylene

The polymerizer off gas showed a marked decrease in the ethylene content compared to the polymerizer feedstock. The off gas had virtually no acetylene in it. The ethane, propylene, propane, butane, and butene content of the off gas was higher than in the feedstock, reflecting the slower polymerization of the higher-molecular-weight olefins and indicating that these compounds are by-products and/or intermediates of the polymerization reaction.

Discussion

The thermal polymerization of olefins to make gasoline was demonstrated to be technically feasible in the 1930s and was commercialized in the 1940s. It still appears to be an option any time that gases can be found which have a significant olefin content. The motor octane tests of today apparently give significantly higher results than the data reported in the 1930s.

The polymerization work performed in this program with pure ethylene may have been misleading with respect to the degree of difficulty in removing the heat of polymerization with purified pyrolysis gases. The latter contain significant amounts of propylene and butylene (which react slower than ethylene) as well as large amounts of diluents; e.g., carbon monoxide, methane, and hydrogen. These diluents serve to reduce the partial pressure of the olefins and consequently to result in a large decrease in the rate of polymerization. It appeared that the limiting factor with the polymerization of the pyrolysis gases was not heat transfer of the exothermic heat of reaction, but rather inadequate residence time. A polymerizer reactor having a tubular inlet (high heat-transfer potential) followed by a soaking chamber (long residence time) may be very desirable, unless the purity of the hydrocarbon stripper product gas were to be greatly improved. This type of composite reactor was commercialized for use with refinery gases.(59)

The product distribution of the polymer gasoline derived from ECO II was very similar to that obtained by polymerization of pure ethylene, as shown by the distillation curves. This is indicative that at the severe conditions in the polymerizer, similar-sized molecules are relatively stable. If it is assumed that the molecular complexity is comparable (i.e., branching, cyclization, and unsaturation), then the octane rating of the ECO II derived polymer gasoline would be comparable to that made from pure ethylene.

Mass balances calculated around the polymerizer using run 75 data indicated that 81% of the ethylene entering the polymerizer reacted in the following manner: 65% reacted to form C_4+ polymer gasoline crude; 11%, to form propylene and propane in a 57/43 ratio, respectively (probably by polymerization to hexene and subsequent chain cleavage to propylene); and 5%, to form ethane. There was virtually no change in the amount of methane (a net loss of 4.5%). Of the hydrogen consumed in the reaction, 93% could be accounted for by the hydrogenation of ethylene to ethane, propylene to propane, and butylene to butane. This would leave very little hydrogen to saturate the higher-molecular-weight polymer gasoline. The acetylene appeared to be very reactive and did not survive the reactor. Presumably the acetylene was polymerizing to form aromatic liquids such as benzene, toluene, etc.

LOW-PRESSURE, CATALYTIC SYNTHESIS AT ARIZONA STATE UNIVERSITY

A small subcontract was let to Arizona State University for the study of low-pressure catalytic conversion of pyrolysis gases to organic liquids.

The final report(60) of this study has been received and reviewed. The intent of this effort was to determine if pyrolysis gases formed from organic wastes could be catalytically reacted to form gasoline at relatively mild temperatures and pressures. The advantages of this approach would be that less compression of the pyrolysis gases would be required and the hydrocarbons would be more easily recovered as gasoline rather than as gases (ethylene). To be successful, this approach requires a very high conversion to liquids on a once-through basis. The approach taken was one of reacting the olefins with carbon monoxide and hydrogen to form a mixture of alcohols and hydrocarbon liquids. This is similar to the Fischer-Tropsch reaction, but is also referred to as the "Oxo" reaction. All feed gases used were purchased bottled gases which were mixed during the experimental runs.

Eight catalysts were screened during the program, including those containing: nickel on silica gel, activated alumina, or kieselguhr; cobalt on activated alumina, kieselguhr, and a proprietary alkaline support; iron oxide on activated alumina promoted with chromium and potassium; and cobalt on kieselguhr promoted with zirconium. Unfortunately, none of these catalysts were deemed as good as the 1:1 mixture of cobalt oxide and activated alumina which had been developed prior to the contract period.

Owing to the exothermic nature of the reactions forming liquids, the catalytic reactor used was of the fluidized bed type, utilizing a 1.83-meter (6-foot) length of 5.08-centimeter (2-inch) schedule 40 pipe made of 316 stainless steel. This fluidized reactor was able to reject the heat of reaction fast enough to maintain stable conditions.

A series of experiments established the optimum reactor temperature at 280°C (536°F) at 862 kPa (125 psia). The effect of increasing the pressure was to linearly increase the rate of liquid formation. A test series was conducted which held the ethylene and carbon dioxide constant in the feed gases at 19.4% and 11.2%, respectively, while varying the hydrogen, methane, and carbon monoxide. It was shown that the liquid formation rate (conversion) increased with an increasing hydrogen content. A relatively small effect on the liquid formation was noted with changes in carbon monoxide levels. In all cases, the ethylene present was consumed in the reaction.

The liquid product formed had a hydrocarbon phase and a water phase. The hydrocarbon phase had about 68% straight-chain paraffins, 27% branched paraffins, and 5% dissolved gases and alcohols. Of the hydrocarbons, 75% were saturated. Because of the large content of saturated, straight-chain hydrocarbons in the product, it was assumed that the resultant octane rating would be low. To upgrade the gasoline product, a reformer using a commercially available catalyst was investigated. The reforming catalyst was operated at 450°C (842°F) and 894 kPa (130 psia). The effect of this catalytic reaction was to convert about one-third of the straight-chain paraffins (having low octane ratings) to aromatic compounds having high octane ratings. Based on the composition of the final gasoline product, an octane number of 80 was calculated.

The water phase of the initial liquid product was found to contain 84% water, 15% n-propanol, and 1% other alcohols. Of all the organic liquid products in both phases, 9.5% was n-propanol. The preferential formation of this particular alcohol is indicative of the "Oxo" reaction involving ethylene, carbon monoxide, and hydrogen. If propylene had been used in the simulated feed gas in the amounts it occurs in pyrolysis gases, a greater amount of butyl alcohols would also have been produced.(61) It is expected that the petrochemical value of the alcohols would exceed their fuel value by a substantial margin if recovered in a purified state; however, they could be added to the hydrocarbon phase after the removal of water.

An examination of the material balance in the report reveals that of the entering ethylene, 79% of it was hydrogenated to ethane, 17% was polymerized to form the organic phase liquids, and less than 1% was reacted to form the propanol in the water phase liquids. Thus, it is seen that the "Oxo" portion of the reaction is very minor. Apparently, the catalyst system used has more of a polymerization and hydrogenation effect on the ethylene rather than one which reacts the carbon monoxide to form significantly more organic liquids. Based on the material balance presented and assuming an 86% gasification of organic wastes, 66 milliliters of organic liquids (including propanol) can be produced per kilogram of dry organic wastes (15.8 gal/ton) or 40 milliliters per kilogram of trash containing 60% dry organics (9.5 gal/ton). As is pointed out in the report, these projected yields are only a fraction of that which would be attained if the "Oxo" reaction were better catalyzed. Alumina has previously been shown to be a polymerization catalyst for propylene at atmospheric pressure and 340°C (about 650°F) and to produce a high octane gasoline.(62) Perhaps the activated alumina used in the catalyst mixture may have acted to polymerize the ethylene, whereas the cobalt oxide acted in a relatively slower reaction to produce the n-propanol. Although both cobalt and alumina can tolerate small amounts of sulfur contamination, it is known that moisture and alkaline contaminants are catalyst poisons for alumina.

In summary, the catalytic conversion of pyrolysis gases to gasoline at moderate pressures and temperatures has been shown to have some technical feasibility. However, the process has several drawbacks compared to thermal polymerization:

1. The complexity of a fluidized-bed catalytic reactor
2. The low octane value of the initial gasoline liquid
3. The need to remove catalyst poisons such as sulfur and nitrogen from the reformer feedstock
4. The production of a small by-product stream of 18% propanol in water (with butyl alcohol contamination) which will require separate distillation and sales effort for optimum marketing
5. The reported low conversion of ethylene to liquids, resulting in an overall low gasoline production unless the resultant large amount of by-product ethane formed were recovered and recycled through pyrolysis. (Optimization of the process subsequent to the contract period has been reported to greatly increase yields to about the same amounts as those projected for the thermal polymerization approach, slightly over 300 milliliters per kilogram of dry organic.)

If this area were to be further pursued, it would be of interest to determine the catalytic effect of alumina without the cobalt oxide catalyst on simulated and actual pyrolysis gases. It would also be of interest to compare preliminary estimates of capital expenditures for the catalytic vs. thermal approach to make gasoline while taking into account that blending of the catalytically formed gasoline with high octane stocks and/or addition of tetraethyl lead may be necessary prior to use by the public. The effect of catalyst poisons suspected to be in solid waste pyrolysis gases would need to be evaluated experimentally for the preferred catalyst.

Although the aspect of catalytically forming petrochemicals such as n-propanol may seem particularly attractive economically, it should be pointed out that by operating at higher temperatures, the thermal polymerization product can be changed from a largely olefinic product to an aromatic one (benzene, toluene, xylene, etc.) having a petrochemical value significantly higher than the gasoline fuel value.(19)(55) The multistep catalytic formation of medium octane gasoline and alcohols has some interesting features, but does not seem to offer overall advantages compared to the thermal polymerization approach to make a high octane gasoline.

SECTION 7

SCALE-UP POTENTIAL

TECHNICAL CONSIDERATIONS

The proposed process to convert organic wastes to gasoline has many similarities to various processes which are now commercialized or which have been in commercial operation in the past. As will be discussed, the area of greatest risk is probably in the area of solids handling of the organic waste feedstock. To reduce risk, it is suggested to scale up to a pilot plant before going to a commercially feasible scale. The pilot plant would be large enough so that it should be sited near at least one easily obtained feedstock; however, data should eventually be obtained with a variety of feedstocks so that the actual site selected would be of secondary importance to the program.

Pyrolysis

The handling of nonuniform waste solids is an order of magnitude more difficult than fluids. The capability of the pilot plant to operate on a wide variety of feedstocks will require a flexible system, to say the least. Part of the design information required would be the characteristics of the potential feedstocks with regard to particle size, shape, moisture, etc. The design of the equipment to fluidize the solid feed would be critical to the success of the pilot plant, since many organic wastes tend to become fibrous when finely ground and are therefore difficult to fluidize. Once the feed is finely ground and fluidized in the grinder, it may be best to keep it flowing. It may be more desirable to multi-train the grinding equipment to have reserve capacity rather than to have a holding bin for the finely ground material.

Once the organic feedstock has been finely ground and fluidized, it will be pneumatically transported to the pyrolysis reactor. The pyrolysis reactor is envisioned as a large number of long, red-hot stainless steel tubes at 700 to 800°C inside of a furnace fired by char and by-product gases. The tube diameter would be less than 10 centimeters as has been common refinery practice.(63) In order to obtain the desired throughput, a multitude of tubes will be placed in parallel as is done by the petrochemical industry when they crack crude oil to make ethylene under similar conditions of temperature, residence time, and level of steam usage.(64) One of the key questions to be answered in the pilot-plant phase would be whether the fluidized solids stream can be evenly divided into a multitude of smaller streams to feed into the individual pyrolysis tubes without plugging.

Historically, an experimental entrained-solids tubular pyrolysis reactor, very similar in concept to that developed for the trash-to-gasoline project, was used in shale oil research and development in the early 1950s. Feeding rates of up to 3.6 tons per day of ground oil shale were attained in this reactor. The equipment used consisted of a screw feeder to meter the shale into the entraining superheated steam flow. The steam-shale mixture then passed through a single Duraloy pyrolysis tube 13 meters (43 feet) long with an inner diameter of 8.6 centimeters (3 3/8 inches). The pyrolysis tube made two complete passes through the gas-fired kiln of firebricks and steel. The pyrolysis temperatures between 540 to 900°C (1000 to 1650°F) were investigated. Flow rates through the system were fairly slow with residence times of 3 to 4 seconds. Cyclone separators were used to separate the spent shale from the pyrolysis gases. The pyrolysis gases had a hydrocarbon distribution very similar to that obtained in this program from ECO II. After passing through a contact condenser, a shell and tube condenser, and a centrifugal mist separator, the gases were compressed to about 715 kPa (104 psia) to allow the condensation of the oil products in an aftercooler followed by a refrigerated condenser. An empirical heat transfer study was conducted which will be very useful in the scaling-up of the trash-to-gasoline pyrolysis reactor.(26)

The materials technology to build the furnace appears to be state-of-the-art, but there is the question of the erosion of the tubes due to the scouring action of the char and dirt which will be in turbulent flow. Although intermittent bench-scale operation at NWC has not revealed a problem of tube erosion, it should be carefully watched in the pilot-plant phase.

Efficient recovery of the energy content of the pyrolysis stream leaving the reactor is dictated by the large amount of steam needed for the process and is commercially practiced in ethylene plants.(65) A high-temperature heat exchanger would be placed to reduce the pyrolysis stream temperature from about 760°C to about 200°C. The pyrolysis stream temperature cannot be lowered much below 200°C without the risk of condensing tar vapors which would foul the heat exchanger surfaces and cause the heat exchanger to plug up. The presence of char and dirt in the pyrolysis stream creates the very high heat transfer rates experienced with fluidized beds and also prevents coke from fouling the heat transfer surfaces. The very fine char is to be removed from the pyrolysis stream in parallel, small-diameter cyclones after the stream has passed through the heat exchanger. The diameter of the cyclones must be kept small in order to retain the fine char.(66) The gas stream is then rapidly cooled by spraying "quench water" into it. This causes the tars to condense into small droplets rather than to adhere to the heat-exchanger surfaces. Part of the hot quench water can be recycled through the heat exchanger as a supply of superheated dilution steam for pyrolysis. The steam will be further superheated in the pyrolysis furnace. Organics carried by the quench water would then be subjected to further pyrolysis. Ultra-fine char entrained in the quench water used for boiler feed water would be subjected to the water-gas reaction in the boiler to form additional hydrogen and carbon monoxide. Hot water from the quench system can be used for process heat to produce hot air for the drying of the feedstock.

This general approach to heat recovery from pyrolysis streams and recycling of the water used to make pyrolysis steam is practiced commercially.(67) The condensed tars and water-soluble organics which accumulate in the quench water can be cleanly incinerated in the pyrolysis furnace with very little impact on the overall energy balance.(68) The disposal and/or recyling of the contaminated quench water will be an important part of the pilot-plant demonstration.

Low-Pressure Gas Cleanup

After the pyrolysis gases are cooled, the small remaining tar mist must be removed prior to compression. This is a relatively persistent tar mist, and a scrubbing tower in conjunction with the quench system is indicated. To increase the degree of cleanup the mist-laden pyrolysis gas stream may need to be electrostatically ionized prior to scrubbing.(69) Bench-scale experience at NWC has indicated that, although a second-stage scrubber followed by a demisting cyclone was helpful, the pyrolysis gas still needed to be filtered before entering the compressor. Unfiltered pyrolysis gases had a tendency to cause the compressor valves to gum up and stick. The cleanup of the pyrolysis stream to remove residual char and tar with well-designed scrubbers will be one of the important aspects of the pilot plant.

To compress the pyrolysis gases from about atmospheric pressure up to above 3100 kPa (450 psig) for storage, a three-stage reciprocating compressor was used at NWC. Pyrolysis-gas-storage pressures of up to 9300 kPa (1350 psi) were used. Normally, very little condensate was recovered from the intercoolers, although significant amounts of aqueous and organic condensates were recovered from the storage tank where the compressed gas was allowed to cool to ambient temperatures. The organic fraction is dark in color, but has a very low viscosity and is conjectured to contain primarily low-molecular-weight aromatics; e.g., benzene, toluene, and xylenes. This organic phase is referred to as "pyrolysis gasoline" in the ethylene industry and is thought to be formed by the polymerization and dehydrogenation of olefins during the pyrolysis operation. This pyrolysis gasoline will have use as the lean oil makeup for the hydrocarbon absorber (to be discussed) and as a high octane (100+) blending component for the final gasoline product. The pyrolysis gasoline would be sent to the lean-oil cleanup distillation column for purification. The aqueous phase of the compressor condensate may have use in the final stage of the gas scrubbing operation.

High-Pressure Gas Purification

The gas-purification section separates the pyrolysis gases into three separate streams: carbon dioxide; by-product gases containing hydrogen, carbon monoxide, and methane; and product gases containing ethylene, propylene, and butylene. The hot-carbonate system was pilot planted in the early 1950s(70) and has been commercialized.(71) Although stainless steel reboiler, valves, and pumps are recommended, the remainder of the hot-carbonate system can be of steel if a small amount of potassium dichromate is used to passivate the solution.(42) To avoid the inadvertent precipitation of abrasive potassium bicarbonate in the NWC bench scale, a solution of only 25% potassium carbonate was selected. This concentration is reported to be nearly as effective as more concentrated solutions that are theoretically possible, but which easily precipitate to plug transfer lines if cooled slightly during system breakdown, or for other reasons. To increase the efficiency of absorption and regeneration, modern installations are reported to add proprietary additives to the carbonate solutions.(48)(49) These proprietary additives may or may not be more effective than the small amount of contamination present in the pyrolysis gases since the bench-scale system worked so well.

The final step in the purification system is the absorption of the olefins into a hydrocarbon oil at about 3075 kPa (440 psi). This approach was developed by the petrochemical industry for purification of gases made by pyrolyzing propane to make ethylene and propylene. As noted previously, with the exception of the presence of carbon monoxide and dioxide, the product distribution of cracked hydrocarbons is similar to that obtained by the rapid China Lake pyrolysis technique with MSW. The absorber oil commercially used had an average molecular weight slightly higher than that of benzene and was an aromatic by-product of the cracking process. When propane was the pyrolysis feedstock, an excess of absorber oil was generated which compensated for losses in the absorber off gas (by-product) and stripper product streams. To prevent the recovery of methane in the product gas stream, the bottom of the absorber was kept at 121°C (250°F) to drive the more volatile methane out of the absorber oil before the oil was sent to the stripper. The stripper was maintained at nearly the same pressure, but the lean oil was heated to nearly its boiling temperature, 232°C (450°F) which boiled off the light hydrocarbons (ethylene, propylene, and butylene). A small portion of the lean oil was continuously distilled to remove gums and tars. This system was scaled up to commercial application and was said to be much less energy consuming than cryogenic purification techniques.(41) Initial operation of the NWC bench-scale hydrocarbon absorber and stripper indicated that if carbon dioxide is not previously removed, it will be readily absorbed by the oil and will thus cause dilution of the product gas. The bench-scale system also demonstrated the need to carefully maintain the bottom of the absorber hot enough to prevent methane and carbon monoxide from entering the stripper. The bench-scale hydrocarbon purification system could be tested further to determine if carbon monoxide will be a problem. A single-stage compressor should be adequate to boost the recovered olefins up to the polymerization pressure of 5170 kPa (750 psi), since this is only a compression ratio of 1.7.

Polymerization

In the early 1930s the petroleum industry began to commercially crack heavy feedstocks in order to make more gasoline. A major by-product of this operation was the production of low-molecular-weight gases such as ethylene, propylene, and butylene. Research soon showed that the by-product gases could be readily polymerized to form even more gasoline. This research was soon commercialized both with catalysis(51) and without(40)(54)(59) and was common apparently until the petrochemical market for olefins developed in the 1950s.

The thermal or noncatalytic approach was selected for the organic-waste-to-gasoline program primarily due to the high ethylene content of the pyrolysis gases. The conditions required to polymerize ethylene with phosphoric or sulfuric acid catalysis are very severe relative to those used to polymerize propylene or butylene. A series of catalytic polymerization reactors with increasingly severe conditions might have to be employed to successfully polymerize the olefins. Also the acid catalyst is tricky to maintain in the active state at the temperature required to polymerize ethylene.(51) In contrast, although the thermal polymerization requires higher temperatures and pressures, it preferentially polymerizes ethylene,(53) which is the major component of the purified pyrolysis gases. Thermal polymerization was chosen early in the program and still appears to be the best method. When one uses an impure, randomly contaminated feedstock such as organic wastes, it is comforting not to have to worry about removing all of the possible catalyst poisons. The scale-up of the thermal polymerizing reactor is expected to have a very low risk, as it would be similar in nature to previously commercialized reactors and probably would consist of a tube and shell heat exchanger followed by a soaker chamber.

Product

The NWC laboratory work confirmed the ease of thermal polymerization with pure ethylene. The 1935-era octane values appeared to be about 10 to 15 units lower than those of today, in that the NWC polymer gasoline had an unleaded motor octane of 90 compared with the 75 to 80 range previously reported. After a single distillation, it appears that the polymer gasoline product will have an unleaded octane rating and distillation characteristics suitable for the expected United States market in the forseeable future. At present United States gasoline consumption rates, the impact of the gasoline produced from organic wastes will be relatively small for quite some time so that there would be no immediate danger of flooding the market and depressing the product value. Although the process can be easily adapted to produce pure ethylene and propylene by purification, alcohols by catalytic hydration, or low-molecular-weight aromatic liquids (benzene, toluene, xylene) by higher temperature polymerization, the market for some of these products would be impacted fairly rapidly and would require considerably more marketing expertise to optimize. Since the transportation costs of the organic waste feedstock will be relatively high, widely dispersed small plants are indicated, and this factor makes the concepts of ease of marketing and local product consumption very attractive. This is particularly true in those areas which have an abundance of organic wastes and which are some distance from oil refineries.

Thermal polymerization of ethylene and other olefins has also been found to produce synthetic oils having excellent viscosity characteristics. For example, the lubricating oils formed by thermal polymerization of ethylene, propylene, 1-butene, 2-pentene, or 1-hexene all had pour points less than -32°C (-25°F). When cracked paraffin wax, consisting primarily of alpha olefins, was used as the feedstock the pour point was -34°C (-30°F) and the viscosity index was 137. Temperatures up to 450°C (850°F) and pressures up to about 17,000 kPa (about 2500 psi) were also investigated and found to require very short residence times of a few minutes to avoid product degradation. Attempts to further thermally polymerize a previously thermally polymerized gasoline fraction resulted in a very low oil yield, indicating that extended residence time in the original polymerization to form gasoline will not significantly affect the oil yields at the moderate temperature of 320°C and extended reaction time of 9.5 hours.(72)

Socony-Vacuum Oil Company found that the noncatalytic batch thermal polymerization of the α-olefins, 1-decene, even in the presence of 35 to 55% hydrogen, carbon monoxide, and mixtures of these gases resulted in good lubricants.(73) This implies that in the probable event these gases were to find their way past the gas purification system into the polymerizer coil, there would be no adverse effect on the oil product. The same workers also found that small amounts of propane-propylene mixtures, n-butane, n-pentane and isooctane had a beneficial effect on the yield and viscosity of the oil product.(74) Likewise small amounts (3 to 5%) of aromatic compounds such as benzene, toluene, xylene, and ethyl benzene were also beneficial to the yield and viscosity of the desirable product.(75) The beneficial effect of these paraffinic and aromatic compounds is of great interest to the trash-to-gasoline process since these compounds are expected to be present to some extent in the polymerization reactor.

The thermal polymerization demonstrated in this program produces a synthetic crude oil that contains about 90% gasoline, an estimated 7% diesel oil, and 3% lubricating oil. This ratio of products can be shifted only slightly by changing the reaction temperature and pressure. The diesel oil will be a relatively undesirable product because of its lower value, $0.092 per liter ($0.35 per gallon), but the synthetic lubricating oil fraction will have a very beneficial impact on the economics due to its relatively high commercial value of about $1.32 per liter ($5 per gallon).(76) If gasoline were to be worth $0.159 per liter ($0.60 per gallon), then the high quality synthetic crude would have a total value of $1.88 per liter ($0.71 per gallon or $30 per barrel). The value of the synthetic oil is about 21% of the total, assuming that it will have the excellent low-temperature viscosity characteristics and thermal stability indicated in the literature for thermal polymerization of similar olefinic feedstocks.(77) For marketing, the synthetic oil (primarily polyalpha-olefins) may need to have about 25% polyester oil added to prevent mechanical seal problems in a manner similar to Mobil Oil's Mobile 1, which retails for $4.24 per liter ($16 per gallon).(76)

The market for by-product oil may be considerably more difficult to exploit than the gasoline market due to public consciousness of the brand names of lubricating oils. Extensive testing will be needed before the by-product oil can be compared with the leading synthetic oils made from chemically pure feedstocks, although fairly simple laboratory tests can easily verify its general suitability as a lubricant.

Utilities

About half of the energy contained in the organic-waste feedstock will be available for process energy. About 28% of the process energy will be derived from the combustion of char, with the remainder from the by-product gas stream. The major shaft energy consuming operations are grinding the feed and compressing the pyrolysis gas. The major thermal energy consuming operation is pyrolysis, because large quantities of low-pressure steam are required to dilute the reaction to optimize the olefin production. It will be very worthwhile to consider, at least for full-scale plants, the cogeneration of low-pressure steam and shaft (electric) power with high-pressure steam. This approach partially expands the "high-pressure" steam in a turbine to "low-pressure" levels where the steam is used in the process.(78) If the low-pressure steam energy is added to the shaft energy obtained, then overall conversions of

90 to 95% are indicated. The NWC bench-scale pyrolysis uses low-pressure steam at 275 to 400 kPa (40 to 60 psi) in the steam ejector. Since the efficiency of turbines increases with size, probably one large turbine to generate electricity would be advantageous over several small turbines in the plant. An alternative would be to heat and then expand the by-product gas in a turbine from its original 3000 kPa (440 psi) prior to its combustion and/or to use the exhaust from a gas turbine to produce steam. In any case, the pilot-plant design stage should carefully evaluate alternate methods of power generation to determine if they would be sufficiently novel to require pilot-plant demonstration or if they should be implemented only in full-scale plants. It is also interesting to note that the by-product gas stream is very similar in composition to that demonstrated to be suitable for use in internal combustion engines.(79) Waste heat recovery would be a key question in any case.

The choice of the carrier gas used to convey the solid feed through the pyrolysis reactor will have a large impact on the utility requirements. The NWC bench-scale system has shown that the choice of the following carrier gases has very little impact on the production of the desired olefins: nitrogen, carbon dioxide, steam, methane, carbon monoxide, and a mixture of hydrogen, methane, and carbon monoxide. The relative quantity of carrier gas used does, however, have a large impact both on the quantity of olefins produced per unit weight of feed and on the utility requirements. The more carrier gas recirculated, the more energy required, although the yield is increased. The olefin yield is apparently a function of the concentration of the pyrolysis products in the reactor, in a manner analogous to the steam cracking of crude oil to make olefins. Since the above-mentioned gases appear to be inert in the pyrolysis reaction, a preliminary trade-off study was made to compare the relative energy to circulate the various gases in the system. This detailed study took into account the shaft and thermal energy required to actually recover and circulate the candidate carrier gas through its entire loop, including process steam. The results of this NWC study are summarized in Table 13. The energy required per standard volume of carrier gas is tabulated in the two right-hand columns of Table 13: one column assumes a 30% conversion of thermal energy to shaft energy (e.g., obtained with complete expansion in a steam turbine), and the other column assumes a topping cycle in which the steam is only partially expanded in a turbine and then is used for low-pressure process steam at an overall system efficiency of 90%. (The topping cycle requires a ratio of process to shaft energy greater than 5 to 1.) The power recovery referred to takes advantage of the high-pressure carrier gases for shaft power generation in a gas turbine. The interesting results of this study are that the use of carbon dioxide as a carrier gas with hot-carbonate recovery is relatively energy intensive and requires three to four times more energy than the use of steam or by-product gases. A possible combination (Approach V) of carbon dioxide and steam in which the steam used to regenerate the carbonate solution in the carbon dioxide stripper is used as a major fraction of the carrier gas showed some promise, but was not quite as good as the use of by-product gas and steam at the same ratio of gas to steam. The CO_2 and steam mixture has the disadvantage of being partially condensable and could give problems in the solids feeder similar to those created by steam.

This study strongly suggests that from energy considerations the use of carbon dioxide as the carrier gas should be questioned. It now appears that

TABLE 13. CARRIER GAS ENERGY COMPARISONS

		Required energy, SMJ/m^3					
		A	B	C	D		
	Carrier gas approach	Preheat to pyrolysis temperature	Heat recovered in desuperheater	Low-pressure steam	Shaft power required	Total energy required with 30% thermal-to-shaft efficiency (A - B + C + D/0.3)	Total energy required with 90% thermal-to-shaft efficiency (A - B + C + D/0.9)
I	CO$_2$ with hot carbonate (no shaft power recovered)	1.48	1.18	4.94	0.86	8.1	6.2
II	Steam	0.98	0.89	1.79	0.00075	1.9	1.9
III	By-product gas (with gas turbine power recovery)	1.03	0.78	0.44	0.27	1.6	0.99
IV	By-product gas (without gas turbine power recovery)	1.03	0.78	0.15	0.53	2.2	0.99
V	0.26 CO$_2$ + 0.74 steam from carbonate stripper (no power recovery)	0.98	0.96	1.34	0.31	2.4	1.7
VI	0.26 by-product + 0.74 steam (without gas turbine power recovery)	0.99	0.86	1.36	0.14	2.0	1.6

plant safety considerations (fire and toxicity) would be the primary advantage of using carbon dioxide for the carrier rather than the flammable and toxic by-product gases. Unless the solid-waste feedstock is maintained above about 100°C, problems with steam condensing in the solids feeder may preclude the sole use of steam as the carrier gas, although the use of steam is very energy and capital cost competitive. (It should be noted that the feedstock temperature will rise to over 100°C while passing through the final grinder and should be fed to the pyrolyzer while still hot, so steam could possibly be used for all of the carrier gas stream.) The best approach appears to be to use the least amount possible of inert carbon dioxide to fluidize and convey the solids to the steam ejector. The major portion of the carrier gas would then be steam. Minimizing the use of the noncondensable carrier gas has the beneficial effect of reducing the size of the compressor as well as the size of the other gas purification equipment. It is interesting to note that the petroleum industry has traditionally used only steam as the carrier (diluent) in the pyrolysis of oil to make ethylene,(29) although a recent advancement in the state-of-the-art by Union Carbide and Kureha Chemical uses a carrier gas composed of superheated steam and carbon dioxide formed by the combustion of hydrocarbon fuels with oxygen.(30)(31)

Materials of Construction

The original pyrolysis system contained parts made of copper tubing, brass fittings, galvanized pipe and "black" pipe, as well as 304 and 316 stainless steel fittings and tubing. The copper tubing was located in the first pyrolysis gas cooler, and the corrosion was so severe that the condensate was discolored by the dissolved copper. The copper tubing was immediately removed and was replaced with a stainless steel heat exchanger.

In the course of making pyrolysis system changes, the entire system was dismantled, which allowed for a qualitative evaluation of the materials problems encountered. Those parts made of 316 stainless steel showed no visible evidence of corrosion, whereas the 304 stainless steel parts (upstream of the condensers, especially) were pitted to varying degrees. The type of pitting was characteristic of chloride corrosion and may be due to the small amounts of chloride suspected to be in the pyrolysis gases. The brass and galvanized steel parts, located downstream of the char cyclone, were coated with a thin deposit of tar, but underneath the tar was no evidence of corrosion. The mild steel or "black" pipes, located even further downstream, were badly rusted and were removed from the system. These qualitative corrosion observations are encouraging in that the substituting of galvanized steel for 316 stainless steel in much of the pyrolysis system could greatly reduce the construction costs of the full-scale system. Latex rubber tubing was used to connect the quench pumps to the cleanup system with periodic replacement being necessary, so that the rubber tubing was converted to 316 stainless steel tubing.

Most of the gas purification system was constructed of 316 stainless steel. Notable exceptions were: the 0.635-centimeter (1/4-inch) ceramic burl saddles used in the absorption and stripping towers, Viton and Teflon seals, and 416 stainless steel check valves. The pressure booster had an aluminum piston and steel walls, and the pressure regulators downstream of the CO_2 scrubber were brass with rubber diaphragms.

The compressor condensates were found to cause Buna-N and Viton O-rings to swell badly, so that Teflon seals are recommended. The rubber diaphragm in the pressure regulator on the compressor recycle loop finally disintegrated, probably because it was in contact with the condensates.

ECONOMIC SCALE-UP CONSIDERATIONS

Municipal Waste Feedstock

To determine the economic feasibility of the process to convert municipal trash into gasoline requires a long list of assumptions. For the use of municipal trash as feedstock, it was assumed that the trash contained 60% dry organic material, 13% inorganics (iron, aluminum, and glass), and the balance moisture. A credit of $4.85 per tonne ($4.40 per ton) of trash processed was assumed for the value of the reclaimed metals and glass. A yield of 45 gallons of hydrocarbon liquids per ton of raw trash processed was assumed and referred to simply as "gasoline". The relative economics of the process were taken to be a function of capital cost, plant size, gasoline (hydrocarbon) value, and the dump fee per ton of trash credited to the process. The plant size can be expressed in terms of the population served by the process, by assuming a daily per capita trash generation rate of 2.25 kg/day (2.5 tons daily per 1000 people).

An in-house preliminary economic evaluation was made by identifying the major equipment items and then using Chilton factors(80) to estimate the installed cost and operating cost.(81) This study indicated that a 91-tonne/day (100-ton/day) plant would involve a capital cost of $6.32 million and an annual operating cost of $815,000 in early 1978 dollars. To verify this analysis, the sponsor (EPA) let a contract to Dow Chemical Company, Freeport, TX, to conduct an independent process evaluation. Dow's preliminary cost estimate for a 91-tonne/day (100-ton/day) plant was $7.6 million capital costs and $873,000 annual operating costs in early 1978 dollars.(82) Most of the 17% extra capital cost identified by Dow was related to process changes that had occurred since the original in-house study had been completed. To obtain extrapolations of the Dow cost estimates, the capital costs were scaled using 0.65 as the exponential scaling factor, whereas 0.20 was used as the labor scaling factor.(83) It is interesting to keep in mind that petroleum prices are widely predicted to inflate at annual rates of 3 to 7% faster than the overall economy, due to the projected increase in deeper wells and offshore rigs needed to maintain oil production rates. At 3% compounded for 10 years, gasoline value would increase by 34%, whereas at 7% annual increase it would double in 10 years. The gasoline value to be considered is the local wholesale value, not the much lower value often quoted at a world-scale refinery located in some large seaport or oil field.

Figure 45 shows the economics for a plant financed at an interest rate of 8% and a 25-year amortization. This would be fairly typical of a municipally financed plant which could be operated either by the municipality or by a contractor. With a $10 per tonne dump fee credited to the plant, a 250-tonne/day plant would produce gasoline costing $0.11 per liter ($0.40 per gallon). Figure 46 shows the economics for the municipally funded situation, but pessimistically assumes

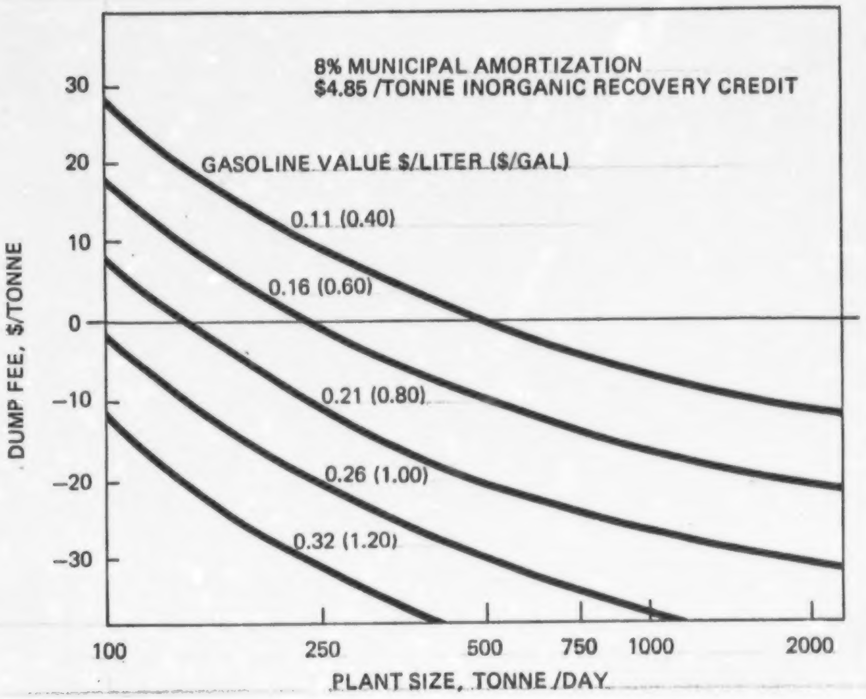


Figure 45. Municipal Trash-to-Gasoline Economics.

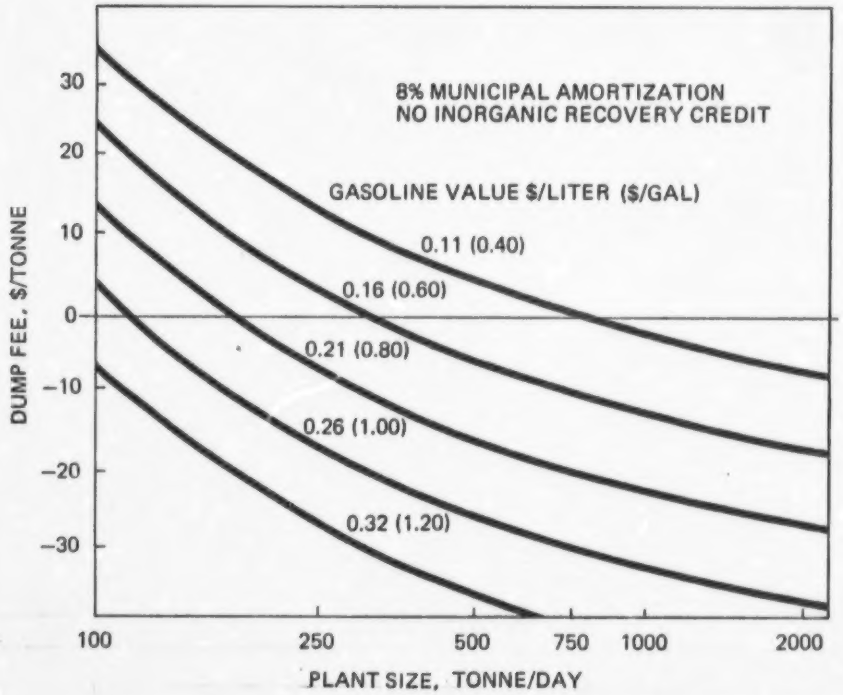


Figure 46. Municipal Trash-to-Gasoline Economics with no Organic Salvage.

that the salvaged metals and glass have no value. For the same 250-tonne/day plant with a $10 dump fee, the cost of the gasoline is seen to increase to $0.12 per liter ($0.46 per gallon). Therefore, the impact of the salvage market on the overall economics is seen to be relatively minor.

Figures 47 and 48 are based on the same assumptions as before, including a reasonable salvage market, but with private enterprise involved at a 15% and a 20% rate of return, respectively. At a 15% rate of return, the small 250-tonne/day plant with a $10 per tonne dump fee must charge about $0.20 per liter ($0.75 per gallon) to meet its financial obligations. For private enterprise, larger plant sizes are clearly indicated. For example, at a 15% rate of return and the same dump fee, a 500-tonne/day plant size is estimated to produce gasoline valued at about $0.13 per liter ($0.50 per gallon). A 500-tonne/day plant required to produce a 20% rate of return or a 5-year payback is shown in Figure 48 to produce gasoline valued at about $0.18 per liter ($0.70 per gallon). As noted before, the larger the plant size, the more economical the gasoline is to produce.

Selecting the 500-tonne/day MSW plant size, the projected rate of return as a function of local wholesale gasoline value is shown in Figure 49 with dump fee parameters. Depending upon the average gasoline value and dump fee assumed for the lifetime of the plant, it can be seen that the economic projections are very favorable at this time and in all probability the economics will improve with time for the reasons outlined in the *Introduction*.

Biomass Feedstock

The process to convert trash to gasoline is thought to be applicable also to agricultural and silvicultural materials. These organics could be a mixture of wastes and/or material specifically grown for conversion to fuel. The assumptions were modified somewhat to reflect the lack of metal and glass recovery equipment and the lack of these salvage products. The feedstock was assumed to contain 90% dry, ash-free organic material. The yield of gasoline per unit weight of organic material was assumed to be the same as with municipal-trash-derived organics. Similar trends are observed with biomass processing plants as with the trash plants. As shown in Figure 50, with financing by 8% bonds, such as might be done by a farming cooperative, a 1000-tonne/day plant could pay $30 per tonne of delivered organics and produce gasoline for sale at $0.17 per liter ($0.63 per gallon).

To interest private capital at a 15% rate of return, the 1000-tonne/day plant could either pay $22 per tonne of delivered organics and charge $0.17 per liter ($0.63 per gallon) or it could pay the same $30 per tonne as the farming cooperative and charge $0.19 per liter ($0.72 per gallon), as can be seen in Figure 51. The effect of requiring a 20% rate of return or a 5-year payback on the biomass conversion plant is shown in Figure 52. With a 1000-tonne/day plant, if the grower were paid the same $30 per tonne of delivered organics, the gasoline would have to sell for about $0.21 per liter ($0.81 per gallon).

These economic predictions point out that, if the process is to be so economical as to afford the organic feedstock, fairly large plants will need to be constructed. However, by most standards these plants at the

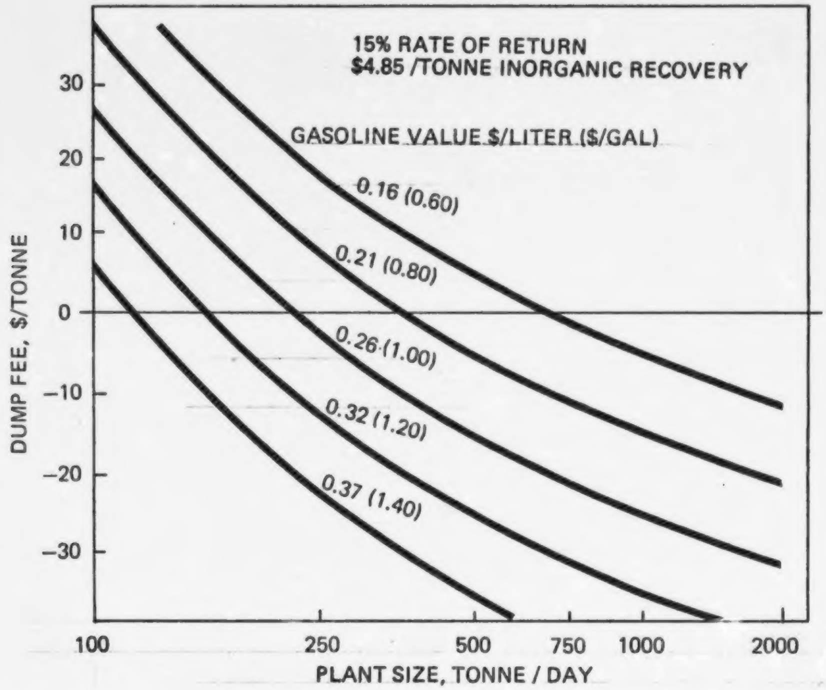


Figure 47. Trash-to-Gasoline Economics at 15% Rate of Return.

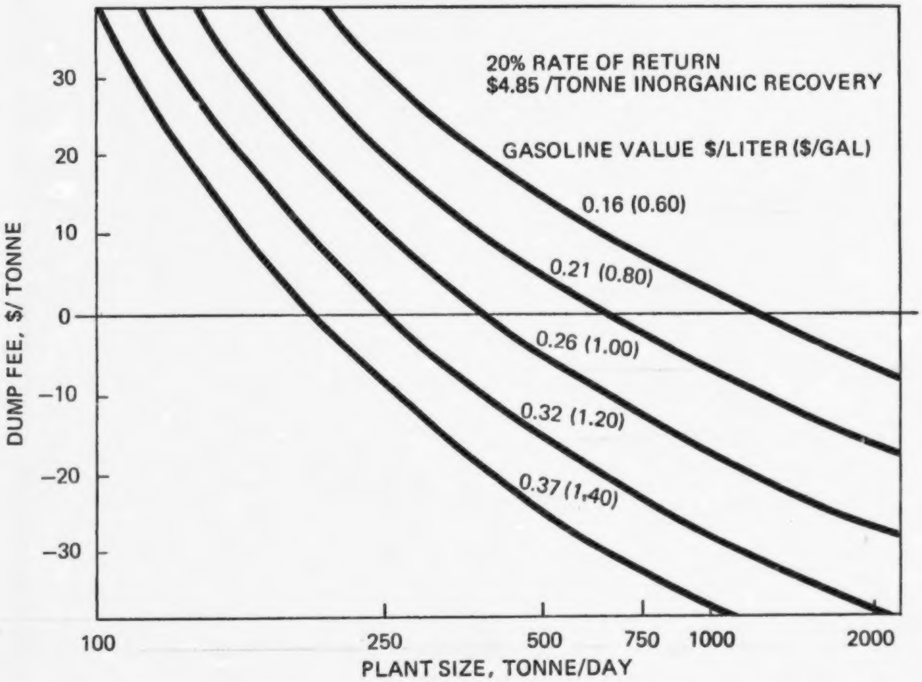


Figure 48. Trash-to-Gasoline Economics at 20% Rate of Return.

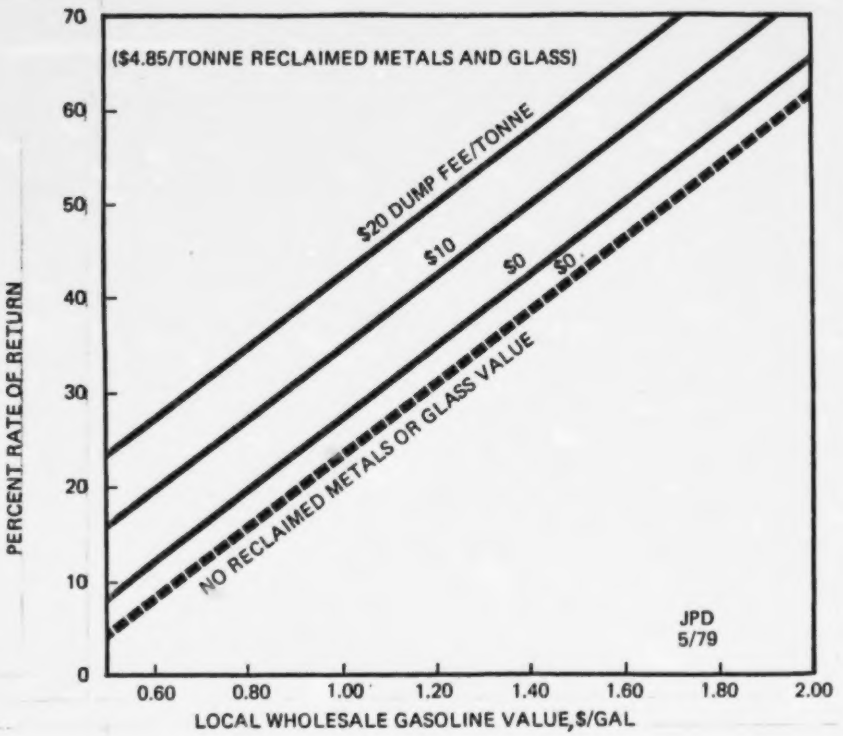


Figure 49. Trash-to-Gasoline Economics: 500 tonne/day.

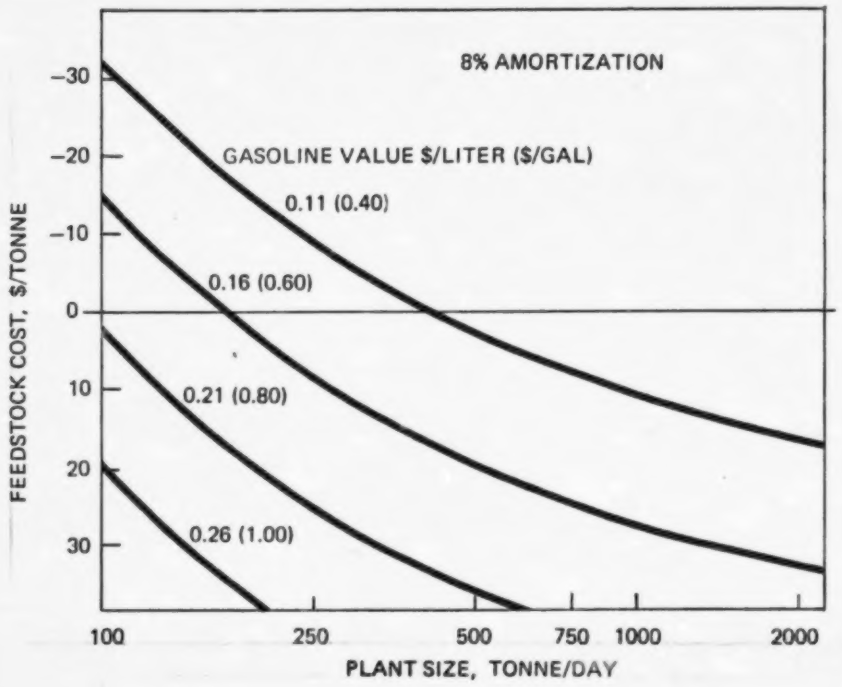


Figure 50. Biomass-to-Gasoline Economics (8% Amortization).

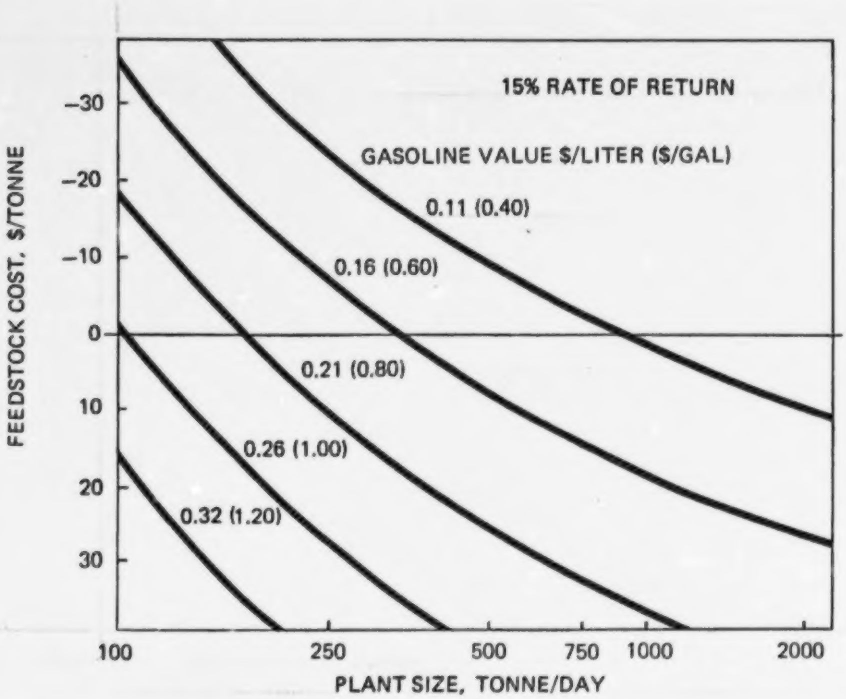


Figure 51. Biomass-to-Gasoline Economics (15% Rate of Return).

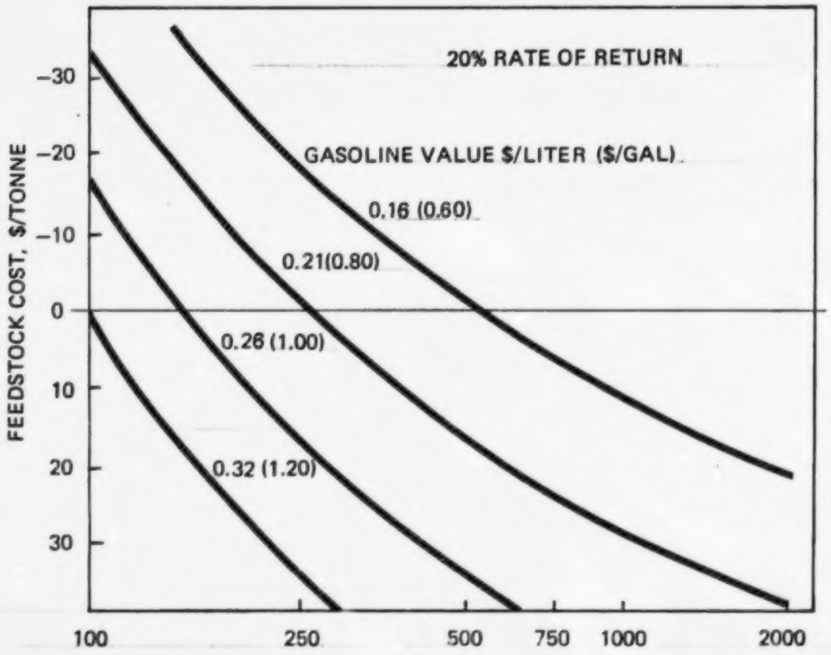


Figure 52. Biomass-to-Gasoline Economics (20% Rate of Return).

1000-tonne/day day size are in reality not very large and would have an output of a fairly small oil refinery (less than 2000 barrels per day). If the 1000-tonne/day biomass-to-gasoline plant were to be located at the center of a biomass-producing area with an assumed annual biomass production rate of 11.2 tonne/ha (5 tons/acre), the necessary biomass could be raised within a 10.2-kilometer radius. Long hauling distances would not seem to be involved with this process, and the gasoline produced would be consumed relatively locally.

Looking at the 1000-tonne/day plant in more detail, Figure 53 shows the rate of return as a function of local wholesale gasoline value with feedstock cost parameters. This size of plant will be very attractive by the time the process can be commercialized.

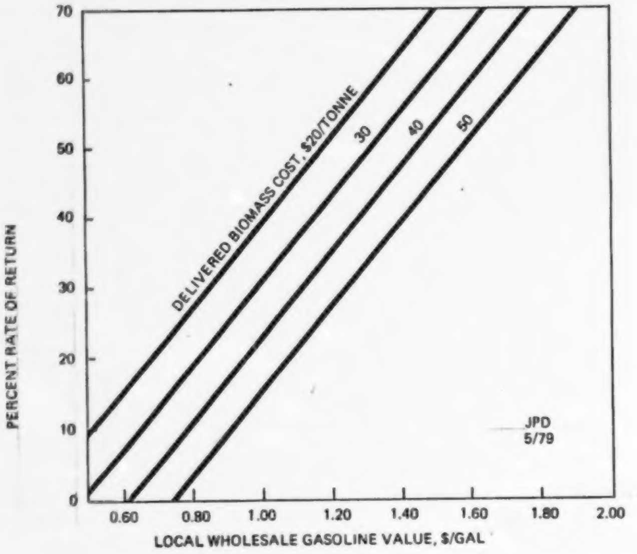


Figure 53. Biomass-to-Gasoline Plant Economics: 1000 tonne/day.

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